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Nutrient Removal from Wastewater by Physical-Chemical Processes

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Jesse M. Cohen

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Environmental Protection Agency
Office of Research and Monitoring
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio
March, 1971

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Jesse M. Cohen**

Introduction

The discharge of biologically treated wastewater effluents into lakes or streams causes eutrophication which is generally attributed to nutrient elements such as phosphorus or nitrogen. Data accumulated during the past 20 years, indicates that increased eutrophication is caused primarily by greater discharges of phosphorus. Control of phosphorus should lead to control of eutrophication. Shapiro (1) states that no claim is made that phosphorus is the sole cause of eutrophication nor that it is always the prime cause. What is claimed is that phosphorus is a "key" element by virtue of the fact that, of all major elements required by fresh-water algae, phosphorus is present in the least amount relative to need. Limiting the availability of phosphorus, therefore, could lead to control of eutrophication. The case for removal of nitrogen, the second of the two key elements in eutrophication, can be made on bases other than eutrophication.

Concern over eutrophication problems has provided the impetus to search for processes which reduce nutrients in discharged wastewater. Considerable effort has been directed toward the development of economic methods to achieve near complete removal of undesirable nutrients. This paper considers the more promising advanced waste treatment methods which have been developed, or are being developed, for removal of phosphorus and nitrogen from wastewater. This discussion is restricted to the physical-chemical processes, although it is recognized that

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biological processes are also being developed. Only domestic or domestic-industrial wastewaters are considered, although the processes described may be equally applicable to industrial waste discharges.

Phosphorus Removal

Forms of Phosphorus

Phosphorus is usually present in wastewater in the form of organic phosphorus, inorganic condensed phosphates and orthophosphates. The concentration of phosphorus in domestic wastewater is often in the range of 7-15 mg P/l. Most of the organically-bound phosphorus compounds are present as particulate organic matter and as bacterial cells. Very little is known about the dissolved organic phosphorus compounds, but these represent only a small fraction of the total phosphorus content. Inorganic condensed phosphates such as tripolyphosphate and pyrophosphate originate mainly in synthetic detergents. Orthophosphate is excreted in urine and is an end-product of microbial degradation of organic phosphates, and of hydrolysis of condensed phosphates. Raw sewage will contain 25-85 percent of the total phosphates as condensed phosphates depending on initial content and degree of hydrolysis occurring in the system. A more complete discussion of phosphorus forms can be found in a committee report of the American Water Works Association (2).

The concentration of total phosphate in raw sewage and the ratio of orthophosphate to polyphosphate vary widely during any 24-hour period. Part of this variation is caused by changes in concentration of orthophosphate but most of it results from a large and rapid increase in polyphosphate during the morning hours, probably the result of home laundry activities. Finstein and Hunter (3) and Laughlin (4) have observed these variations of total phosphate concentration and ratio of ortho to polyphosphate. The data are shown in Fig. 1. To obtain effluents with low phosphorus content in any treatment process the differing forms and the change in forms during the day must be considered. In practical terms, any process must be capable of removing both ortho and polyphosphate forms.

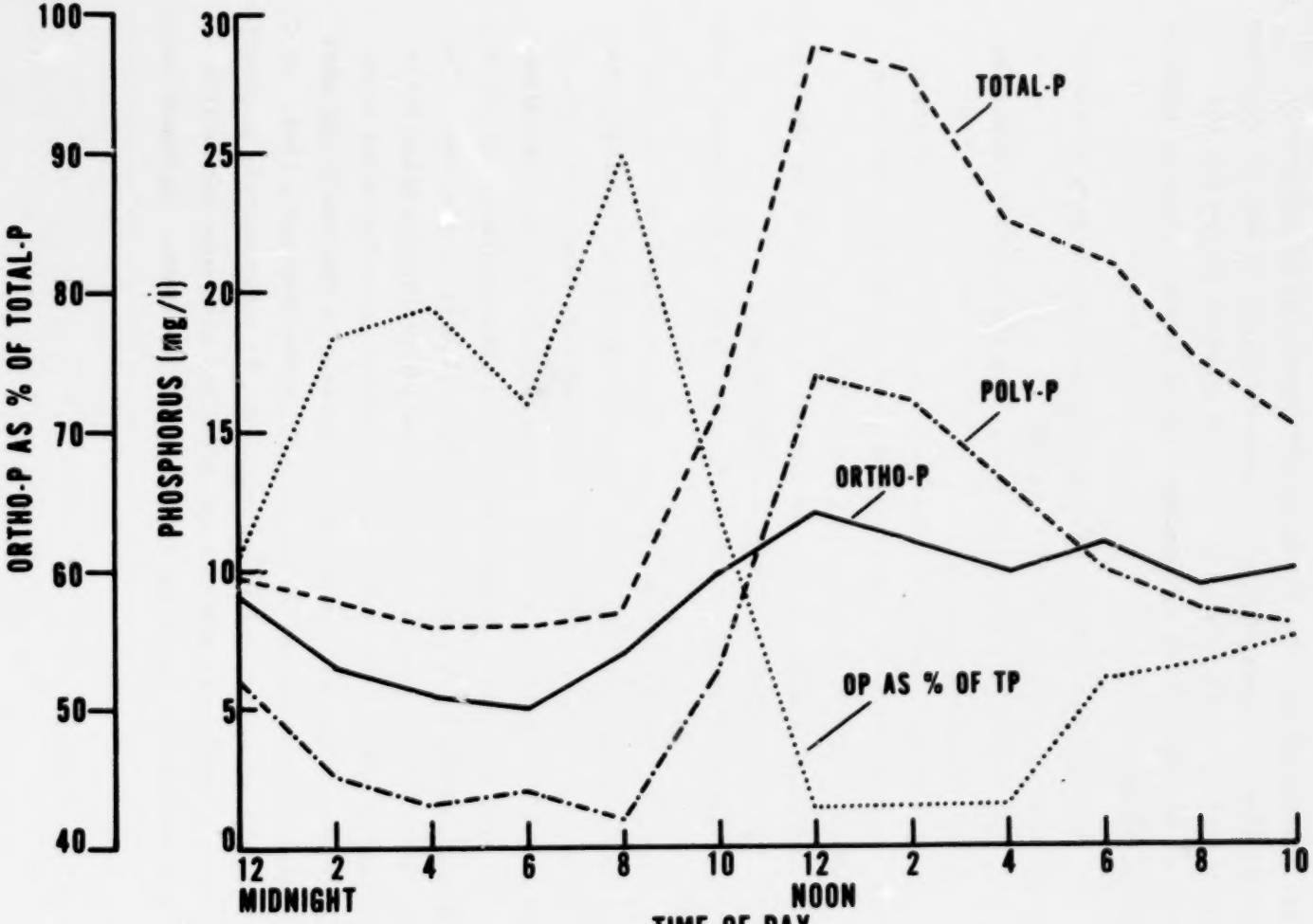

FIG. 1

TEMPORAL VARIATIONS IN THE CONCENTRATIONS OF PHOSPHATE SPECIES (Ref. 3)

General Considerations

The most economic and reliable method of removing phosphates is chemical precipitation. The status of the technology of phosphorus removal by chemical precipitation has been described by several excellent reviews (5)(6)(7)(8)(9). The choice of the chemical to use and the location of its addition in a treatment system depend on several considerations including:

1. The influent phosphorus concentration and the form of the phosphorus at the point of treatment.
2. The degree of phosphorus removal required and the efficiency of the various processes.
3. Characteristics of the wastewater at the point of addition.
4. Compatibility of the phosphorus removal process with other processes in the overall treatment scheme.
5. Sludge handling facilities and ultimate disposal of the sludge.
6. Chemical costs including transportation.
7. Effect of additional mineralization from the precipitant anion.

The above considerations have been discussed in detail by Culp (10).

A variety of chemicals can be used for precipitation of phosphate. Various salts of iron are effective. These include ferrous chloride or sulfate, ferric chloride or sulfate and waste pickle liquor. Aluminum salts are also effective. Commercial alum (aluminum sulfate) is the most widely used aluminum salt, although sodium aluminate is also used. The latter, while more expensive, contains some excess caustic which helps to maintain pH while contributing less inorganic ions than other salts. Lime as a precipitant is very attractive because of its cheap unit cost and because lime sludge can be calcined to recover reuseable lime. At the same time the organics are also incinerated. If recarbonation is practiced with lime, no additional minerals are added and with some wastewaters with high hardness, a reduction of minerals is obtained. Lanthanum salts

are effective precipitants, but the unit cost of the chemical requires that lanthanum be recovered for reuse; however, effective methods for recovery of lanthanum have not yet been developed. All of the precipitants may require the addition of polymeric flocculant to obtain effective settling and separation of solid from liquid. Combinations of chemicals have been found effective; for example, lime plus iron or aluminum salts may be cheaper and yield less sludge than use of either alone. The relative merits of chemical precipitants have been discussed by Malhotra, et al. (11).

The precipitant for phosphorus removal may be added at any point in a treatment system. In any treatment system, there are three basic choices where the chemical may be added, as shown in Fig. 2. While variations on these basic schemes are possible, essentially precipitant can be added to raw sewage as shown in scheme (a), with separation of solids in a settling tank. The effluent may be further treated by biological or physical-chemical processes. In scheme (b) chemical is added to the aeration basin and sludge is removed along with the waste activated sludge. In scheme (c) the chemical is added as a final step in any biological process. For high phosphate removals, a filtration step may be necessary.

Addition of chemical directly to the raw sewage is the location of choice in physical-chemical treatment systems and has substantial merit for biological systems. Addition at this point in the treatment not only removes phosphates but obtains clarification, thus providing suspended solids and BOD-COD removal, all at the same time. With effective clarification, 60-80 percent of the COD is removed thus reducing the organic load to any subsequent process. Furthermore, precipitated phosphate not captured in the settling process will be removed by the subsequent processes which include activated sludge, trickling filter or carbon adsorption. This approach can yield removals of phosphate in excess of 95 percent when adequate dosages of chemical are added. This process also eliminates the cost of a separate primary sedimentation tank.

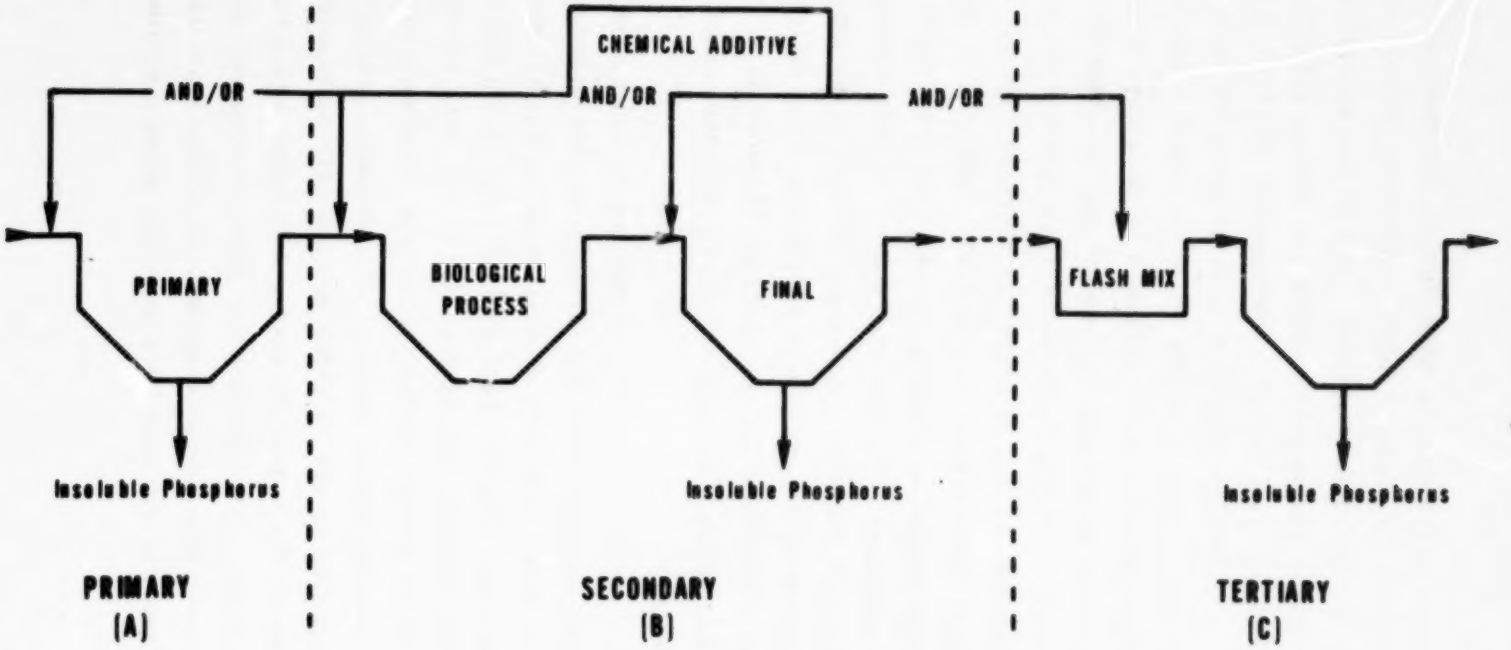

FIG. 2

LOCATIONS FOR CHEMICAL CONTROL OF PHOSPHORUS

Addition of the chemical to aerators in the activated sludge process involves the least capital cost. The only additional capital cost is for chemical storage and feeding equipment and additional sludge handling capacity. This process, however, is limited to the use of iron or aluminum salts, since pH restrictions limit the use of lime; moreover, removals much in excess of 80 percent cannot be obtained consistently.

For high removals of phosphate in an existing biological plant, chemicals may be added as a tertiary process where no restrictions apply as to kind of precipitant. This mode of addition has less appeal and is not widely practiced. The capital costs are high since, in most cases, a filter is required to achieve high removals of phosphate.

Aluminum Salts

The removal of phosphates by aluminum salts such as aluminum sulfate (alum) or sodium aluminate is technically and economically feasible. The removal of precipitated phosphates is accomplished in conventional coagulation and flocculation equipment, followed by sedimentation or filtration. Despite considerable research, the basic chemistry and the mechanism of the removal has not been thoroughly established. Lea, et al. (12) have suggested that removal of phosphates involves its adsorption on precipitating aluminum hydroxides. But according to Stumm (13), Cole and Jackson (14), and Henricksen (15) the interaction of aluminum with orthophosphate results in the formation of an insoluble aluminum phosphate precipitate. The current consensus is that the interaction of aluminum with orthophosphate results in the formation of an insoluble aluminum phosphate. The excess aluminum required to achieve high removal of phosphate, forms hydrolysis products which also react with a small proportion of phosphate.

The overall reaction for phosphate removal by alum can be expressed by the following equation:

$$Al_2(SO_4)_3 + Na_2HPO_4 + 3\ H_2O \text{ ------> } Al(OH)_3 \cdot AlPO_4\downarrow + Na_2SO_4 + 2H_2SO_4$$

The stoichiometry is only approximate and has been shown to be dependent upon pH (11)(13)(16). In practice, and even under optimum conditions, the amount of aluminum salts required for complete precipitation of phosphates exceeds the stoichiometric requirements. On the basis of certain solubility considerations and equilibrium data, the pH of minimum solubility for $AlPO_4$ was calculated by Stumm (13) to be 6.3.

In an investigation of the chemistry of precipitation of phosphates by iron and aluminum salts, Recht and Ghassemi (17) showed that minimum solubility of $AlPO_4$ occurred at pH 6. The relationship between residual orthophosphate and pH when a 2:1 cation to orthophosphate molar ratio was used is shown in Fig. 3. On either side of the optimum pH, increased residual phosphates are obtained and the settling characteristics of the precipitate become poor. Complete removal of the precipitated aluminum phosphate can yield a residual phosphate of 0.1 mg P/l. In practice, however, complete precipitation does not occur nor is the precipitate completely removed; thus practical residuals of phosphorus tend to range 0.2 to 0.5 mg/l.

To obtain complete removal of phosphates to the limit of the solubility of aluminum phosphate requires that an amount of aluminum ion be added in excess of the stoichiometric amount in order to coagulate the precipitate. Hence, in practice, molar ratios of 1.2 to 2.0:$Al:PO_4$ must be added. This relationship is shown in Fig. 4. The data, taken from Recht and Ghassemi (17), show that at a constant pH of 6, the removal of phosphate is directly proportional to the amount of added aluminum up to a ratio of about 1.6:1 Al^{+++}/PO_4^{-3}. The existence of such a linear relationship between the amount of added aluminum and the phosphate removal obtained over such a wide range of added aluminum is offered as evidence that the reaction involves precipitation rather than a heterogeneous mechanism involving adsorption. From the slope of the straight line portion of the curve, it can be calculated that approximately 1.4 moles of Al^{+++} are required for precipitation of 1 mole of orthophosphate.

Many investigators (13)(17)(18) have shown that aluminum salts are

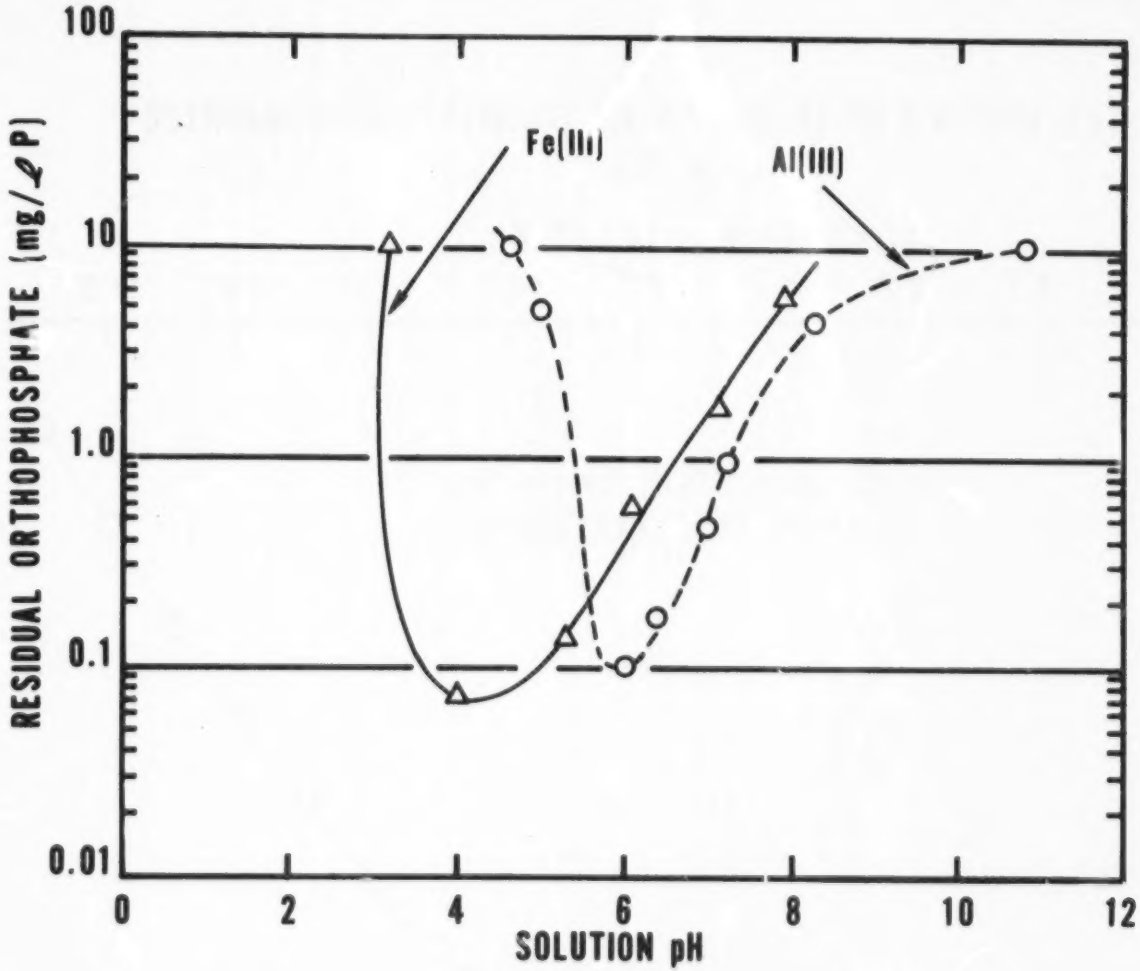

FIG. 3

PRECIPITATION OF ORTHOPHOSPHATE WITH Al (III) AND Fe (III) AT A 2:1 CATION-TO-ORTHOPHOSPHATE MOLAR RATIO (Ref. 17)

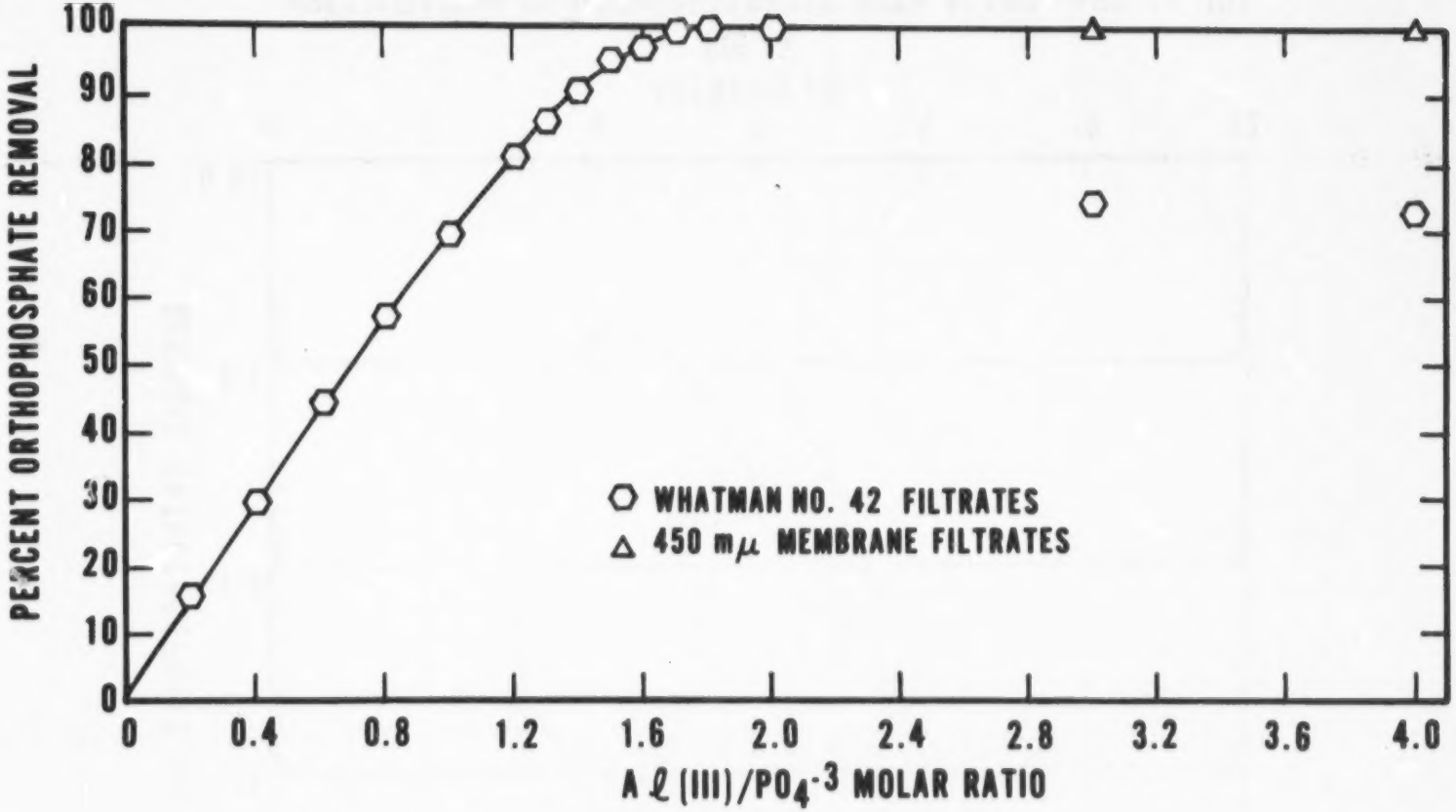

FIG. 4
ORTHOPHOSPHATE REMOVAL BY A ℓ (III) AT pH 6.0 (Ref. 17)

inefficient precipitants for polyphosphates. To obtain removals equivalent to that for orthophosphates, an excess of precipitant must be added. The effect of various polyphosphates on alum dose is shown in Fig. 5; the sewage control sample required 80 mg/l of alum to achieve maximum removal of phosphate. Increased amounts of alum, in excess of 120 mg/l were required when polyphosphates, equivalent to an increment of 4 mg/l P, were added. Similar results were obtained by Recht and Ghassemi (17). This would suggest that in practice, somewhat greater amounts of alum would be required when precipitating phosphate from raw sewage (since polyphosphate concentration is higher) than when alum is added as a tertiary process where substantial hydrolysis of the polyphosphates has occurred during biological action. Extent of hydrolysis of polyphosphates during biological treatment has been described by Finstein and Hunter (3) and by Heinke and Norman (19).

Iron Salts

The chemistry and use of iron salts for phosphorus removal parallel that of aluminum salts with the important difference that divalent as well as trivalent salts are available. The low cost of ferric salts and a history of use going back to the thirties have tended to make iron salts a commonly used precipitant.

As with alum, the reaction of iron with phosphates is pH sensitive. Recht and Ghassemi (17) have shown that the pH of maximum precipitation of phosphate occurs at pH 3.5 to 4.5 for ferric iron. This relationship is shown in Fig. 3. On either side of this pH range, decreased removals of phosphate are obtained. At a constant pH of 4.0, the removal of phosphate is directly proportional to the amount of added iron up to a molar ratio of 1.2:1 $Fe(III)/PO_4^{-3}$, as shown in Fig. 6. This linear relationship, as with aluminum, suggests that a precipitation reaction is involved. A precipitation reaction was also postulated by Gorchev and Stumm (20). In practice, phosphate removal is not executed at the optimum pH and the amount of precipitant is generally dictated by the dosage required to obtain a settleable floc. The need to add more metal ion than is required

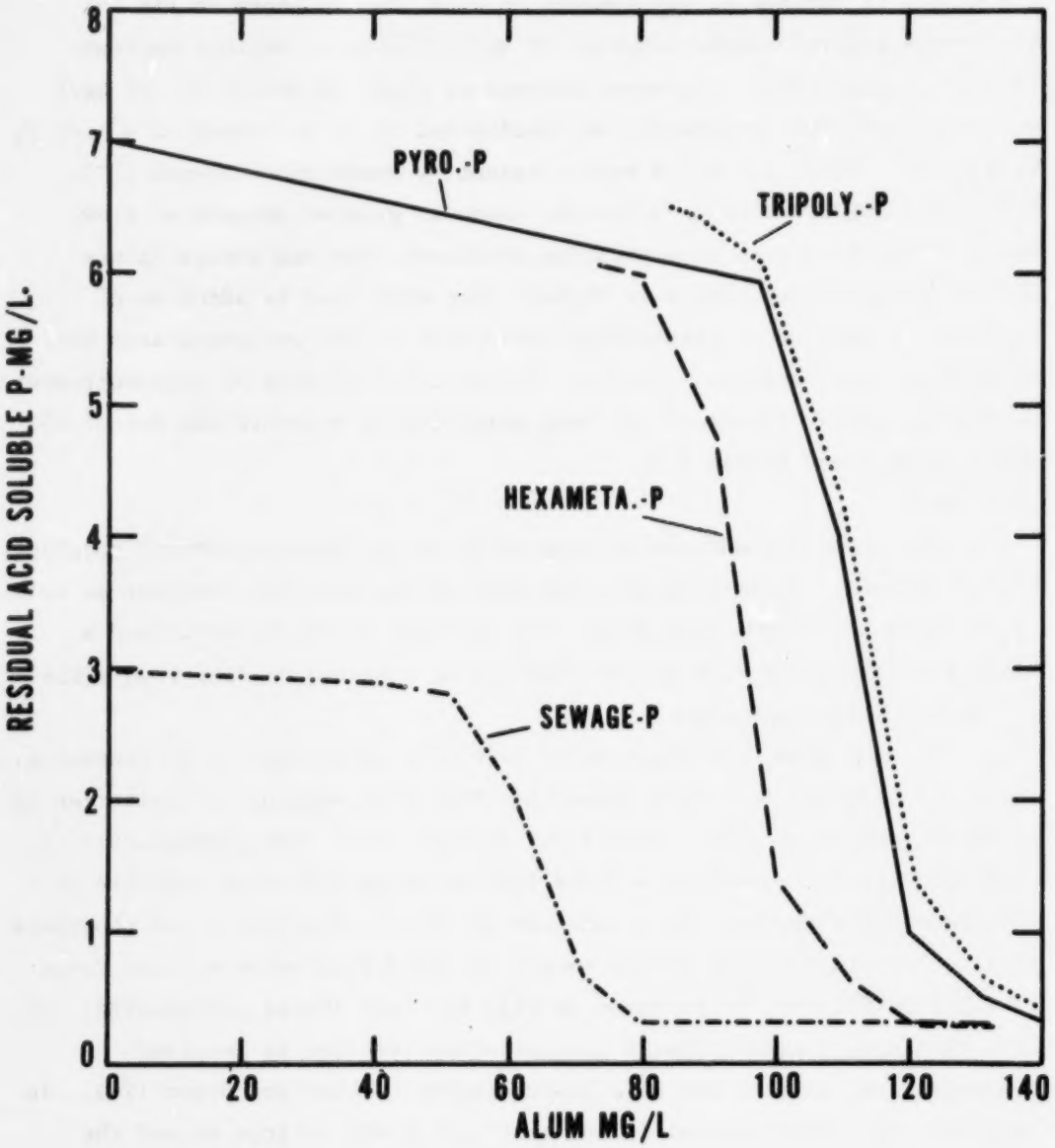

FIG. 5

REMOVAL OF PHOSPHATES BY ALUM PRECIPITATION (Ref. 18)

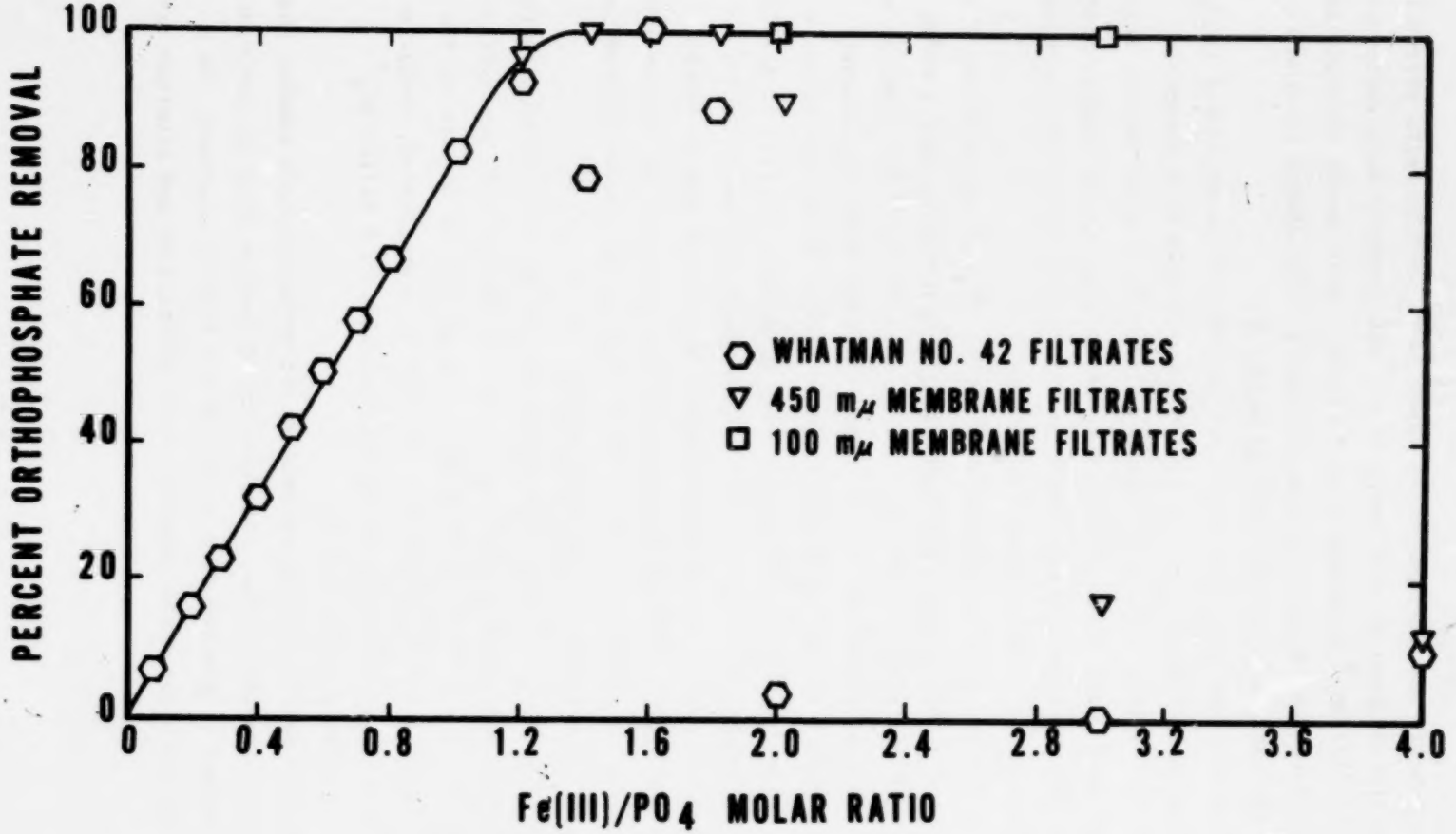

FIG. 6
ORTHOPHOSPHATE REMOVAL BY Fe(III) AT pH 4.0 (Ref. 17)

by stoichiometry was pointed out by Pöpel (21). Ferric salts precipitation is generally obtained at a pH range of 6-7 and requires mole ratios of 1.2-2.0 Fe(III)/PO_4^{-3} to obtain clarification. Both ferric chloride and ferric sulfate have been used interchangeably. The choice is usually made on the basis of cost and ease of handling.

The availability, frequently at low cost, of waste pickle liquor has generated an interest in the use of ferrous iron as a phosphate precipitant. Pickle liquors containing either ferrous sulfate or chloride have been used. The pickle solution contains some excess acidity along with 6-9 percent iron content. Most of the iron is in ferrous form with some undetermined proportion of ferric iron.

In theory, with ferrous salts a dosage of 2.70 mg Fe(II)/mg P is required for orthophosphate precipitation in contrast to only 1.80 mg Fe(III)/mg P for ferric salts and 0.87 mg Al(III)/mg P for aluminum salts. This theoretical advantage of ferric and aluminum salts is, however, partially offset by the greater tendencies of the ferric and aluminum ions to hydrolyze, thus requiring addition of excess Fe(III) or Al(III). Another advantage is the more favorable pH range for use of Fe(II).

Under contract to the Environmental Protection Agency (EPA), Ghassemi and Recht (22) have investigated the chemistry of ferrous iron precipitation of phosphates. Their data have revealed some interesting comparisons with ferric and aluminum salts.

1. The pH of maximum orthophosphate removal with ferrous salts occurs near pH 8 in contrast to Fe(III) and Al(III) precipitation at pH near 4 and 6 respectively. At pH 7.9, 94 percent of the phosphate and 97 percent of the iron is precipitated, either as the ferrous phosphate or as the hydroxide with Fe(II)/PO_4^{-3} equivalence ratio of 1.0.
2. At the respective optimum pH for orthophosphate removal and on an equivalence basis, the capacity of ferrous iron for orthophosphate removal is greater than either ferric iron or aluminum. On a concentration basis, however, both ferric iron and aluminum ion

are more effective precipitants. From Fig. 6, an $Fe(III)/PO_4^{-3}$ equivalence ratio of 1.2 precipitates ≈ 96 percent of the initial orthophosphate. This represents a dosage of only 2.16 mg Fe(III)/mg P, well below the dosage of 2.70 mg Fe(II)/mg P to obtain similar phosphate removals. A similar calculation using available data (Fig. 4) shows that 1.30 mg Al(III)/mg P is required to precipitate 95 percent of orthophosphate under the same test conditions at an $Al(III)/PO_4^{-3}$ equivalence ratio of 1.5. The greater equivalence capacity of Fe(II) for orthophosphate removal and its higher pH of maximum effectiveness may be attributed to its lesser tendency to hydrolyze as illustrated by comparing solubility equilibria for each of the metals:

$$Fe^{+2} + 2\ OH^- = Fe(OH)_2,\ K_{sp} = 5 \times 10^{-15}$$

$$Fe^{+3} + 3\ OH^- = Fe(OH)_3,\ K_{sp} = 10^{-36}$$

$$Al^{+3} + 3\ OH^- = Al(OH)_3,\ K_{sp} = 10^{-32}$$

3. Rates of reaction of Fe(III) or Al(III) with orthophosphate are very fast, < 1 second, but the reaction rate is generally slow, minutes, with ferrous salts. The results of carefully controlled laboratory tests (22) are shown in Table I which summarize some of the characteristics of ferrous iron precipitation. The optimum pH for both phosphate and iron removal is within a narrow pH range around 8.0. Below pH 8, phosphate is poorly removed and residual iron in the product is high. At pH's greater than 8.0, phosphate removal is poor but no residual iron is present.

Practical experience with ferrous salts has, in general, confirmed results from the laboratory. Use of either lime or caustic has generally been required to maintain a pH near 8.0. Thus Wukasch (23) found in full-scale tests that typical requirements for the ferrous chloride system were 10-25 mg/l Fe(II) and 30-40 mg/l of strong base alkalinity as $CaCO_3$ (24-32 mg/l of NaOH or 17-22 mg/l CaO). The greater solubility of ferrous hydroxide can lead to high residuals of iron following precipitation.

TABLE 1

REMOVAL OF ORTHOPHOSPHATE
BY Fe(II) PRECIPITATION[a] (22)

Initial pH	Percent Removal	
	P	Fe
6.0	7.1	8.9
7.0	34.6	38.9
7.9	94.1	96.6
8.9	68.8	≈ 100
10.0	18.3	≈ 100

(a) Initial orthophosphate conc. = 12 mg/l P;
initial ferrous iron conc. = 32.4 mg/l Fe

In practice, dosages of Fe(II) in excess of those required for phosphate precipitation should be avoided and pH should be maintained near 8.0 by increasing the alkalinity. It may also be necessary to add sufficient dissolved oxygen to rapidly oxidize slightly soluble ferrous hydroxide to the very insoluble ferric hydroxide.

The final choice of metal precipitant will depend upon the total cost of all added chemicals required to achieve the desired degree of treatment as well as any incremental costs incurred for conditioning and disposal of sludges.

Coagulation of Precipitate

High removal of phosphates in a treatment plant depends on the completeness of separation of the precipitated metal phosphate from the liquid. To achieve this, metal in excess of stoichiometric requirements is generally added to provide for coagulation of the solids which can be removed by sedimentation. Since precipitation is rarely practiced at the optimum pH for precipitation, a variable proportion of precipitate is extremely fine and resists sedimentation, thus it is common practice to add an anionic polyelectrolyte to aid in the flocculation of the formed

precipitates. And since sedimentation tanks rarely operate ideally, some metal phosphate will appear in the effluent. The amount, of course, will vary with design, operation and dosage of chemical. To obtain residuals of phosphate less than about 0.5 mg/l P requires some additional solids removal process. In practice, this can consist of a granular media filter, carbon contactor or biological aeration process.

Lime

The effectiveness of lime in removing phosphorus from raw and treated wastewaters is well established (11)(24)(25)(26)(27). The chemistry of lime precipitation is entirely different from the chemistry of the hydrolyzing metals such as iron or aluminum. With the latter metals dose is related to phosphate content and the requirement to provide enough hydrolysis products to effect coagulation of the precipitated solids. In contrast, lime requirements for phosphate removal is independent of the phosphate content and is largely a function of the pH and alkalinity of the water. This dependency of lime dosage has been widely observed (28)(29)(30)(31). Lime reacts with the alkalinity to form calcium carbonate and to release hydroxyl ions which lead to increase in pH. Excess calcium then reacts with orthophosphate to precipitate insoluble calcium hydroxyapatite. Additionally, at pH's greater than about 9.5, magnesium hydroxide will begin to precipitate until the reaction is essentially complete at pH 11. An additional reaction in the process is the adjustment of pH to remove excess calcium ion. Carbon dioxide is the chemical of choice. The series of reactions can be shown as follows:

1. $Ca^{++} + HCO_3^- + OH^- \text{-------} > CaCO_3 + H_2O$
2. $5\ Ca^{++} + 7\ OH^- + 3\ H_2PO_4 \text{----} > Ca_5(OH)(PO_4)_3 + H_2O$
3. $Mg^{++} + 2\ OH^- \text{------} > Mg(OH)_2$
4. $Ca^{++} + 2\ OH^- + CO_2 \text{------} > CaCO_3 + H_2O$

Theoretically, the lime dose for any wastewater could be computed from stoichiometry and knowledge of the wastewater's characteristics. However, this approach is rarely used, and the usual method is

to add lime to achieve some desired pH. Thus, use of lime to precipitate phosphates requires a knowledge of (a) desired degree of removal of phosphate, (b) alkalinity of the wastewater, and (c) lime dosage to achieve some desired pH. Fig. 7 illustrates the interdependency of alkalinity, pH and lime dose (28). The lime dose to achieve a pH of, say 11, will range from less than 100 mg/l as CaO for a low alkalinity water, 22 mg/l alkalinity, to as high as 400 mg/l for a high alkalinity water, 600 mg/l alkalinity. The other variable that must be determined is the pH that provides the desired removal of phosphate. Fig. 8 shows the relationship between pH and residual phosphate after filtration. The curve shows that removal of phosphate is continuous and begins when the pH rises to about 9.0 and is substantially complete at pH $\approx$ 11.0. The choice of pH is determined by the desired residual phosphorus. Thus, at pH 9.5, the lowest pH providing any substantial phosphorus removal, the residual phosphate is about 1.5 mg/l as PO_4 (0.5 mg/l P). At pH > 11.0 the residual phosphate is about 0.3 mg/l as PO_4 (0.1 mg/l P).

As pH is increased beyond pH $\cong$ 9.5, the product water becomes saturated with calcium ion resulting in high concentrations at pH's above 11. This excess calcium hardness generally must be removed to prevent post-precipitation. In practice, two types of lime treatment are employed. Single-stage treatment, in which the wastewater is treated to some pH value and then discharged with no further treatment, is generally applicable with high alkalinity-high hardness waters and where desired residuals of phosphorus can be obtained at relatively low pH's - $\cong$ 9.5. At higher pH's, two-stage treatment is required. In the two-stage process, lime is added to some high pH - $\cong$ 11.0 and the precipitated solids are separated. The product from this stage is treated with carbon dioxide to reduce the pH to $\cong$ 9.5 which precipitates the excess calcium as calcium carbonate. Two-stage lime precipitation is clearly more costly than single-stage but is required for high removals of phosphorus and where excess hardness is undesirable. Details of two-stage lime precipitation have been described by Stamberg, et al. (28).

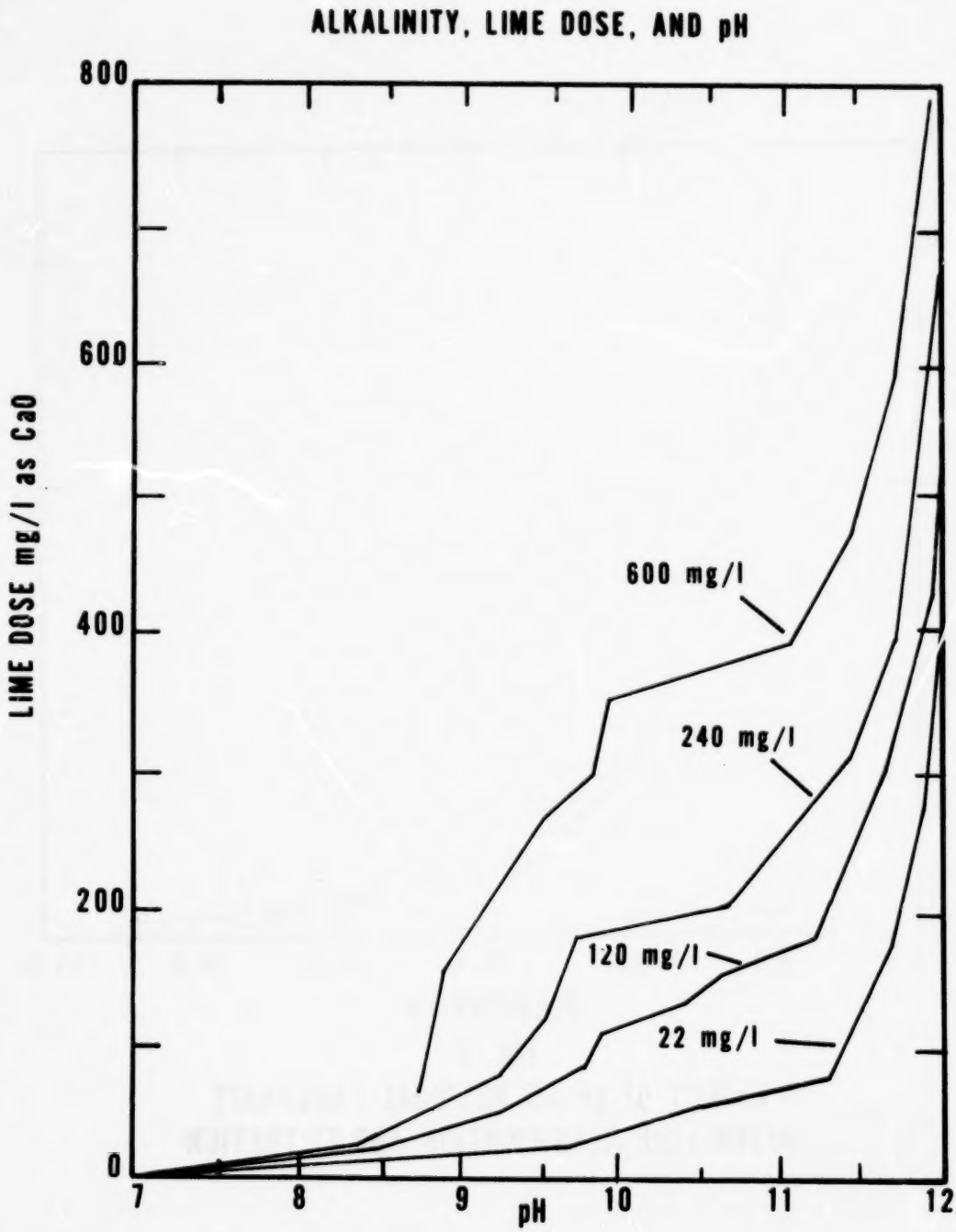

FIG. 7

RELATIONSHIP BETWEEN ALKALINITY, LIME DOSE AND pH (Ref. 28)

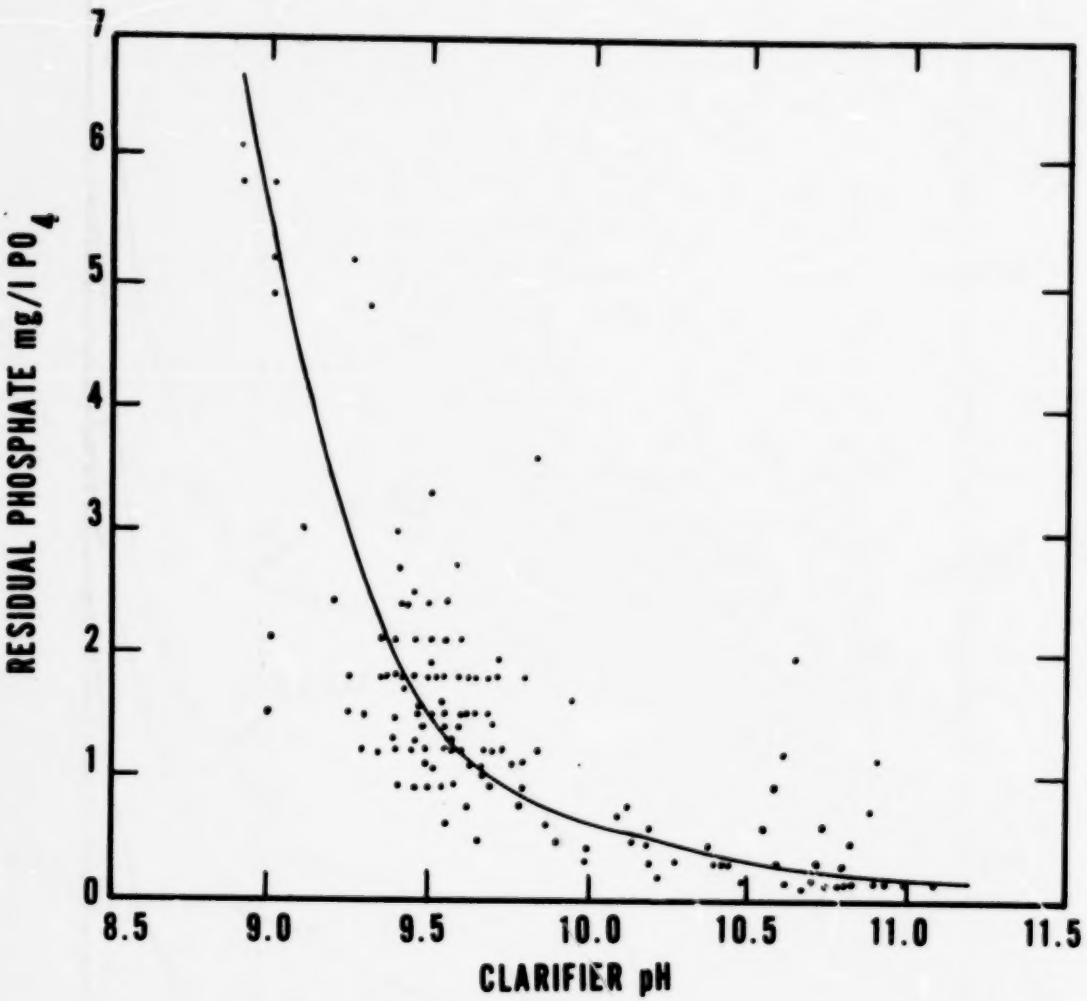

FIG. 8
EFFECT OF pH ON RESIDUAL PHOSPHATE
AFTER LIME CLARIFICATION AND FILTRATION

One of the advantages to the use of lime is that sludge from the process can be calcined which incinerates the organic matter and converts the calcium carbonate and hydroxide to reuseable calcium oxide. The calcium phosphate remains as inert material and is periodically wasted to remove calcium phosphate from the system. Details of lime recovery and reuse have been described by Mulbarger, et al. (30). Rand and Nemerow (32) and Slechta and Culp (24) have reported that recalcined lime can be used for phosphate precipitation.

Chemical Cost for Phosphorus Removal

The chemical cost for phosphorus removal will vary widely depending on the choice of chemical, the dose required and the process used. Albertson and Sherwood (33) summarized chemicals cost using data reported in the literature. The data, shown in Fig. 9, indicate that costs for chemicals can range from as little as $20 to as high as $80 per million gallons to achieve an 80-95 percent reduction of phosphate. To these costs must be added the cost of additional equipment, labor and disposal of sludge.

Other Removal Processes

Lanthanum

One of the rare earth metals, lanthanum, has been shown to be an effective precipitant for phosphate by Recht and Ghassemi (34). They demonstrated that, with secondary effluent, lanthanum was a superior precipitant to iron and aluminum in four principal ways: (1) lanthanum was effective over a wide pH range, pH 4.5 to 8.5 in contrast to a pH range of 5.0-6.5 for aluminum and pH 3.5-4.5 for iron (III); (2) lanthanum precipitates polyphosphates equally as well as orthophosphates; (3) the reaction of lanthanum with phosphate is stoichiometric and requires little excess to obtain a settleable precipitate; and (4) almost total removal of phosphates can be obtained, < 0.1 mg/l residual P. Fig. 10 illustrates these advantages over aluminum as a precipitant. At a 1:1 cation to orthophosphate molar ratio, nearly complete removal of phosphorus is obtained over a pH range of 5.0 to 9.5. Under the same conditions, aluminum removed barely 60 percent of the phosphorus. Analyses of filtrates from precipitation

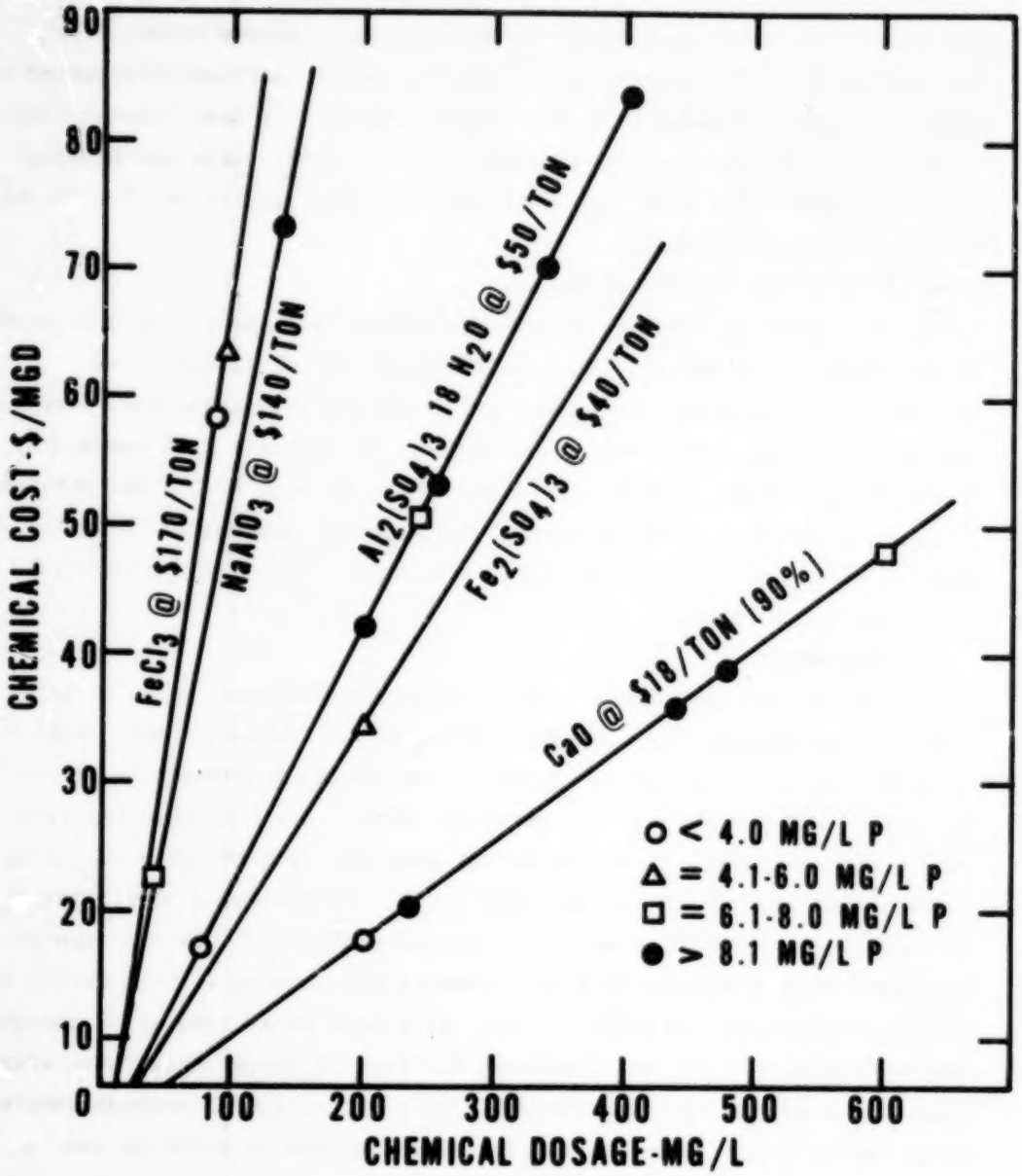

FIG. 9
CHEMICAL COSTS FOR PHOSPHATE REMOVAL (Ref. 33)

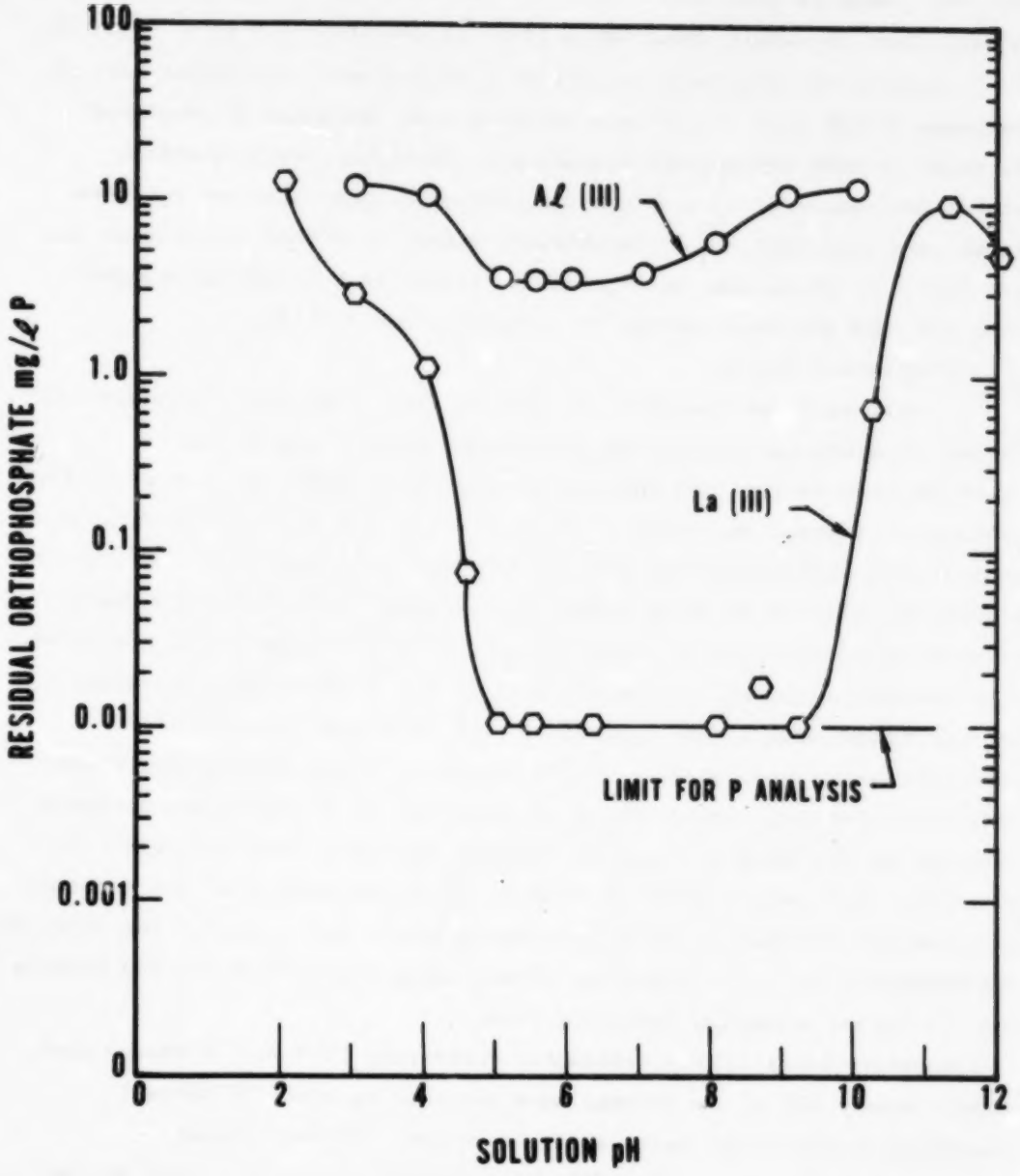

FIG. 10

COMPARISON OF La(III) AND Aℓ (III) PRECIPITATION OF ORTHO-P AT 1:1 CATION TO ORTHOPHOSPHATE MOLAR RATIO (Ref. 34)

of phosphate by lanthanum showed that excess lanthanum was removed along with the lanthanum phosphate. Residual lanthanum was not detectable using an analytical procedure which had a limit of detectability of 0.5 mg/l La.

Despite its clear superiority as a precipitant, the higher cost of lanthanum versus iron or aluminum requires that lanthanum be recovered for reuse to make the process economically feasible. While chemical methods for recovery of lanthanum are available, they have not yet been proven, and practical use of lanthanum remains restricted. Lanthanum may find use as a "polishing" precipitant to remove last traces of phosphate after the bulk has been removed by iron, aluminum or lime.

Activated Alumina

Anion exchange reactions on aluminas have long been recognized (35). The use of activated alumina for phosphate removal, however was first proposed by Yee (36) who removed phosphate compounds from a low-level radioactive process wastewater. Development of the process for phosphorus removal from wastewaters was described by Ames and Dean (37). The removal process is achieved by using common ion-exchange techniques. The wastewater is contacted with activated alumina in a two-stage column contactor. When phosphorus appears in the effluent of the first column, the alumina is regenerated with sodium hydroxide. The mechanism for removal of phosphate remains uncertain. From a kinetics study, Winkler and Thodos (38) concluded that removal could be described by an adsorption mechanism, although on the basis of reaction enthalpy changes, Ames and Dean (37) concluded that removal probably occurred by a combination of ion exchange and chemical reaction. The difference, however, may be due to the differing pretreatments of the alumina; the former using nitric acid treated alumina and the latter using the hydroxide form.

Laboratory tests (37) on wastewater containing 10.3 mg/l P showed that approximately 400 column volumes were required to reach 10 percent phosphorus breakthrough using a single column. If two columns were operated in series, more than 600 column volumes could be loaded on the first column before regeneration was required. Elution of phosphorus was

accomplished with 8 column volumes of 1 M NaOH followed by 20 column volumes of wash water. The 8 column volumes of regenerant containing the phosphorus, organic matter and HCO_3^- can be treated with lime. The phosphorus is removed as calcium hydroxyapatite and the HCO_3^- as calcium carbonate. Most of the organic matter is removed along with the solids, allowing reuse of the NaOH (37).

Use of activated alumina ion exchange process has some advantages over precipitation. The process is selective for phosphate ion (and arsenate) and will remove both ortho and polyphosphates. The process can be controlled to produce effluents with < 0.1 mg/l of phosphorus. Use of alumina produces no pH change in the product, and no additional inorganic ions are added. The process appears to be unaffected by feedwater composition.

The results of the laboratory study on activated alumina were essentially confirmed in a pilot plant mounted in a trailer (39). The system consisted of a multimedia filter to pretreat the secondary effluent, three alumina columns, and facilities for lime treatment of the regenerant solution. Two of the alumina contactors were operated in series while the third column was being regenerated. Typical breakthrough curves are shown in Fig. 11 which represents the last in a series of phosphate loading operations. At that point, approximately 465,000 gallons had been processed with 98 percent phosphorus removal.

Activated alumina for phosphorus removal has not yet been applied at full scale. Acceptance by the field awaits demonstration of its performance and cost. As with lanthanum, it seems likely that activated alumina may find its greatest use as a "polishing" process because of its capability of near complete removal of phosphorus. Yee (36) estimated that about 20,000 column volumes of a waste containing about 0.3 to 1.0 mg/l P could be processed to 1 percent phosphate breakthrough in the effluent. Under these conditions, essentially complete removal of phosphorus can be obtained at reasonable cost.

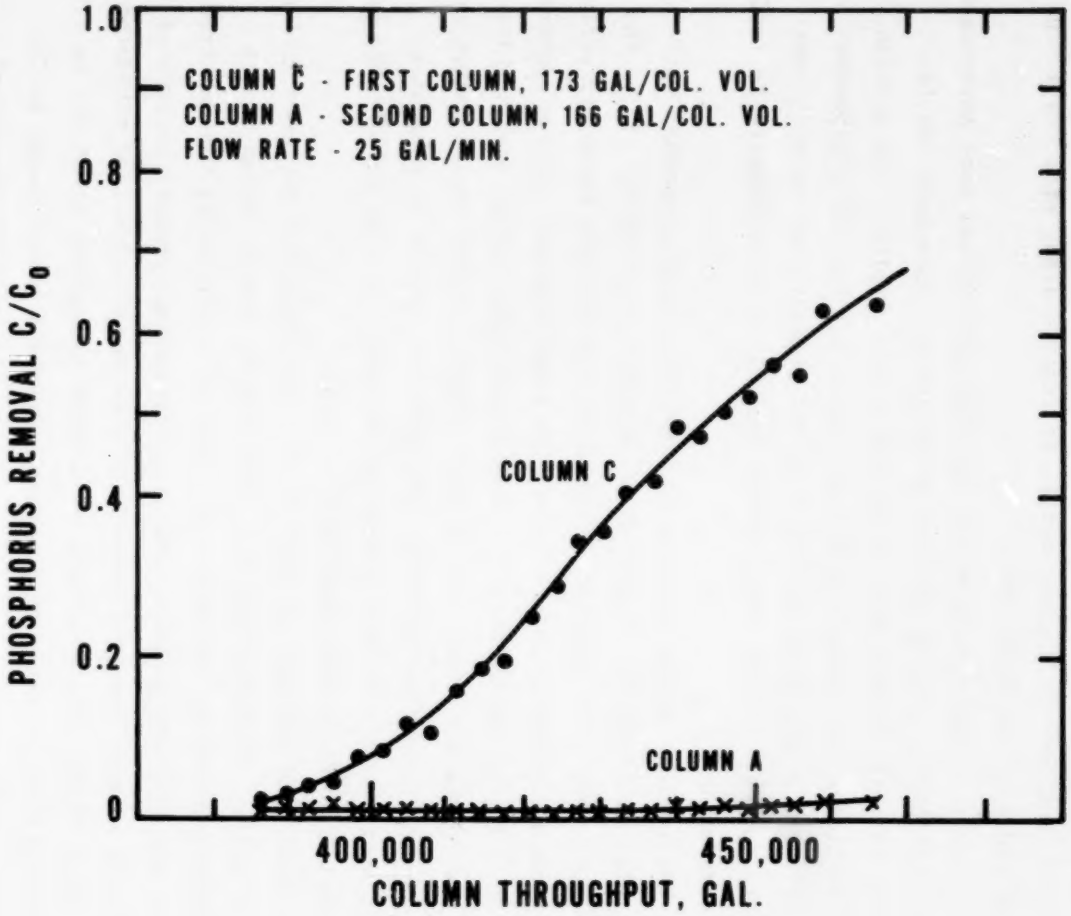

FIG. II
REMOVAL OF PHOSPHATE BY TWO-STAGE ALUMINA COLUMNS (Ref. 39)

Nitrogen Removal

Forms of Nitrogen

Approximately 90 percent of the total nitrogen entering a waste treatment plant is in the form of ammonia. The principal origin of ammonia is urea which is rapidly converted to ammonia by the enzyme urease. The remaining 10 percent is in the form of more complex organic compounds (40). Total nitrogen concentrations in secondary effluents have been reported to range from 12 to 42 mg/l as nitrogen.

In addition to serving as an algal nutrient, ammonia nitrogen in effluents is undesirable for other reasons: (1) ammonia consumes dissolved oxygen during oxidation to nitrates, (2) reacts with chlorine to form chloramines which are less effective as disinfectants than free chlorine, (3) is toxic to aquatic life, (4) is corrosive to certain metals and (5) affects chlorine demand at downstream water plants.

Biological processes are being developed to remove nitrogen. Ammonia can be nitrified biologically to nitrate which then is biologically denitrified to nitrogen gas. These processes will not be discussed here.

Physical-chemical methods to remove nitrogen forms from wastewater are in various stages of development. The best developed processes are: (a) ammonia stripping, (b) natural zeolite ion-exchange, and (c) breakpoint chlorination.

Ammonia Stripping

The ammonium ion is very soluble and stable in water and is the principal nitrogen form in raw wastewaters at normal pH's. Ammonium ions exist in equilibrium with ammonia and hydrogen ions as shown by the following equation:

$$NH_4^+ \leq\cdots\cdots\cdots

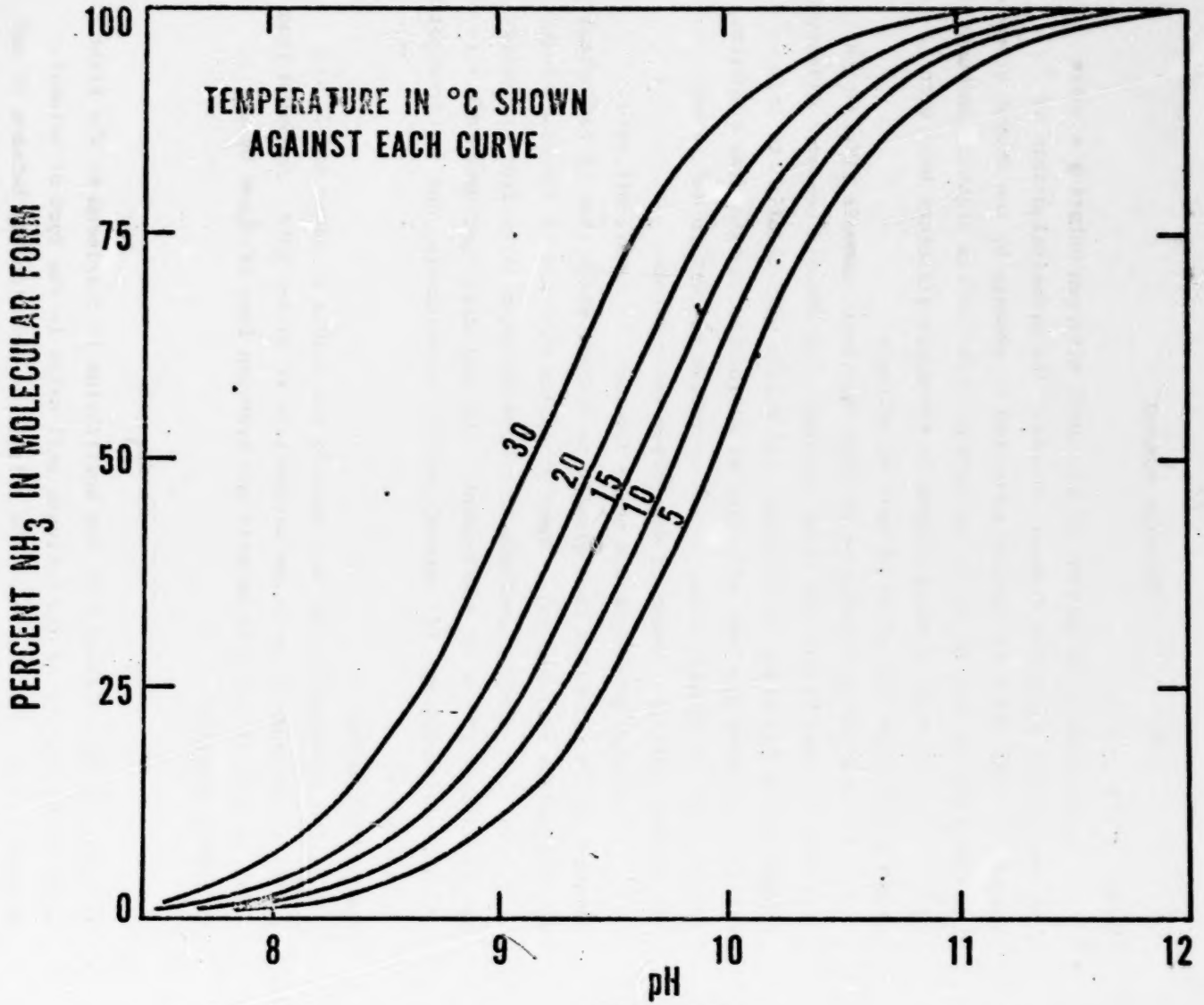

FIG. 12

RELATION BETWEEN pH AND PERCENT AMMONIA

the temperature decreases. Now, since ammonia is volatile, it can be removed by contacting the water with air. The first requirement of a practical process is to adjust the pH. From Fig. 12, at any pH above 10.5, and at a temperature higher than 10°C, 90 percent of the ammonia is available for removal by air stripping. Early studies by Kuhn (41) of feasibility of stripping of ammonia from wastewater revealed a major difficulty. Because of the high solubility of ammonia in water the volume of air required to strip a unit volume of water was very high - about 500 ft^3/gal to obtain 92 percent removal of ammonia at a pH of 11 in an experimental tower packed with Raschig rings. Bayley (42) has shown that the use of traditional types of packing such as Raschig rings results in excessive pressure losses and consequently very high power consumption.

The problem of high power cost, associated with a packed tower, was solved by investigators at the South Lake Tahoe Public Utility District and reported by Slechta and Culp (24), who used a tower packed with redwood slats such as is used for cooling water. The pressure drop across such a device is very low - about 1/2 inch of water - so power costs are reduced to reasonable levels. This tower was used principally to evaluate the effect of aeration at various pH's. The results of this study are shown in Fig. 13.

Optimum ammonia removals at pH values above 9.0 were obtained with an aeration time of about 0.5 minute or, with this particular tower, at an air/liquid loading of about 750 cubic feet per gallon. This study clearly showed that removals of ammonia in excess of 90 percent could be obtained if the pH was maintained above about 10 and if high air-to-liquid volume was applied.

Based on the results of these tests, a 25 foot high tower filled with redwood slats was constructed. Secondary effluent was treated with caustic soda to pH 11.5, and fed to the tower. Water and air was contacted in a countercurrent mode. Results of this work are shown in Fig. 14. For a given supply of air per gallon of wastewater, the efficiency of ammonia stripping increased with increasing packing depth. Efficiencies of the

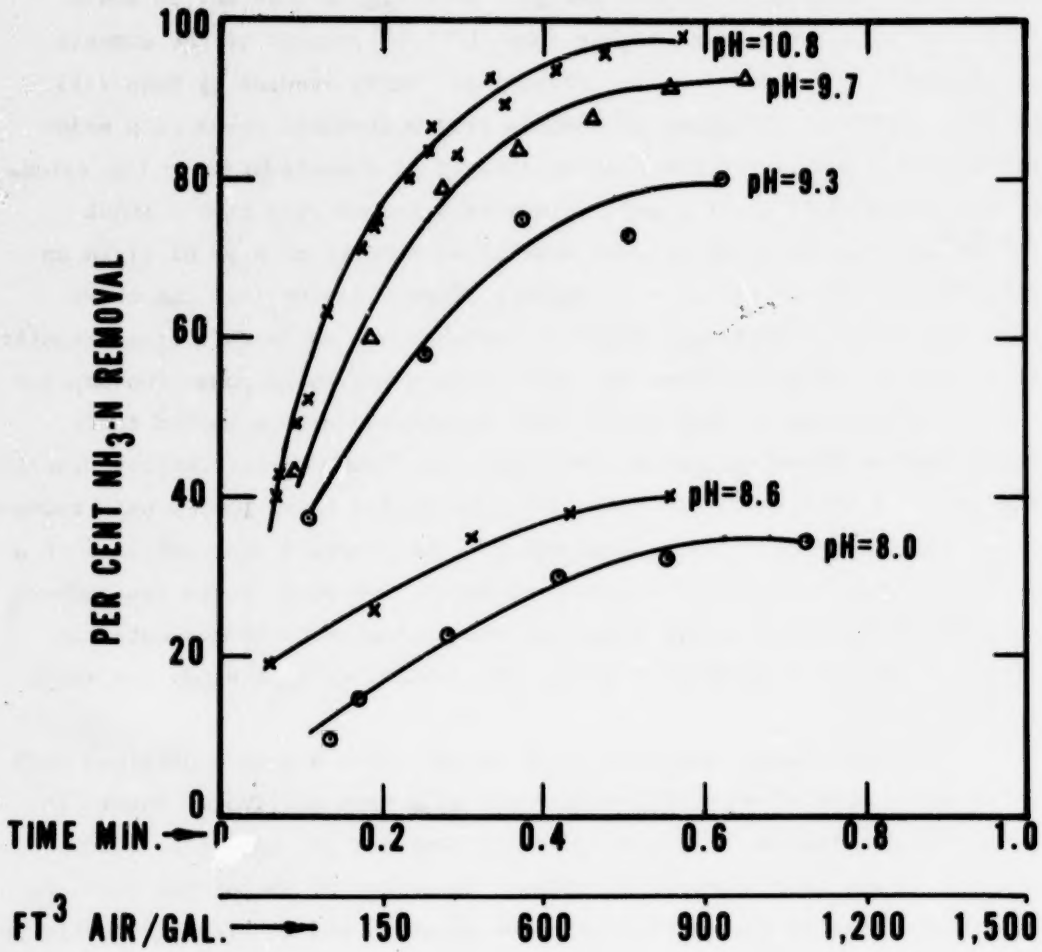

FIG. 13
PER CENT AMMONIA REMOVAL VERSUS AERATION TIME (Ref. 24)

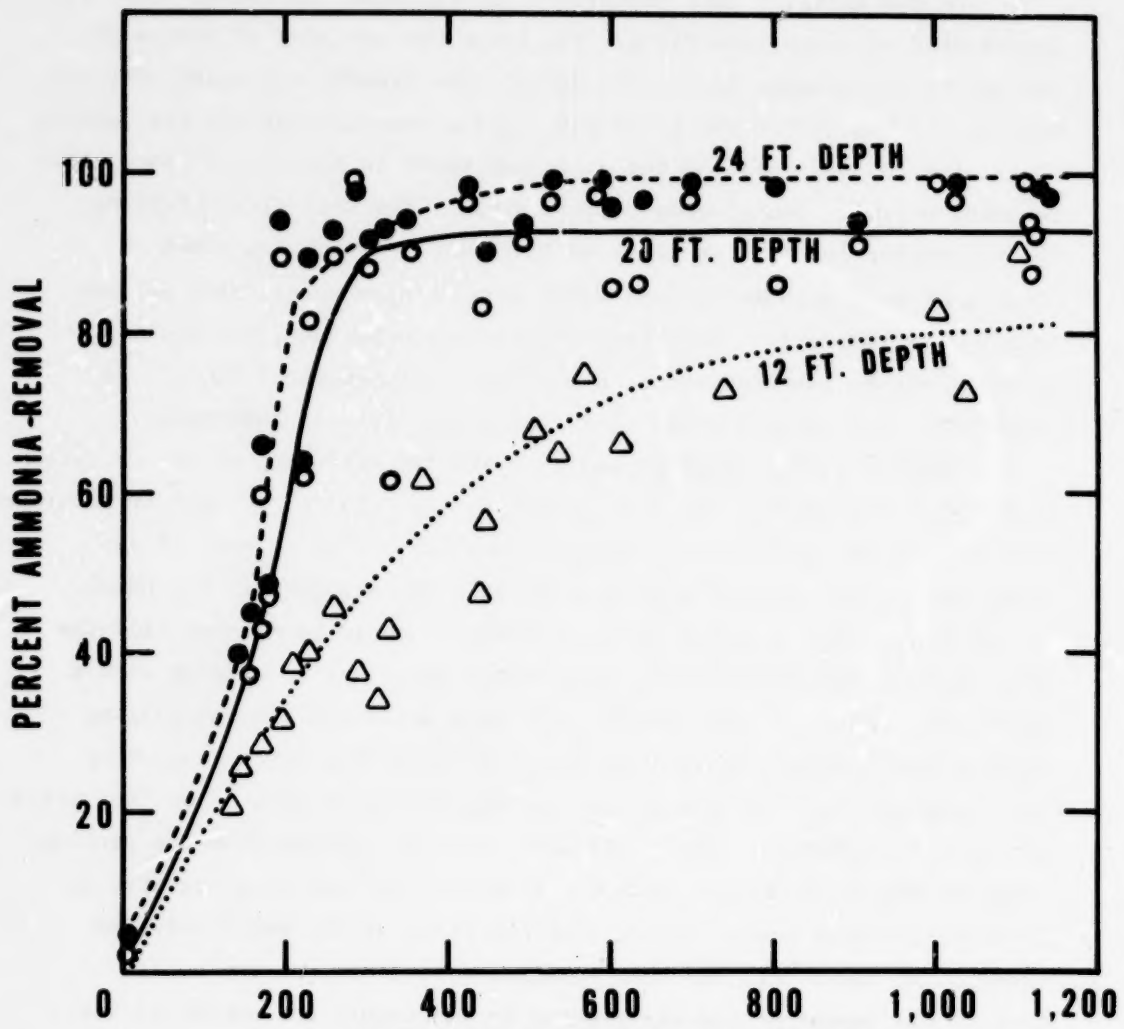

FIG. 14

PERCENT AMMONIA REMOVAL vs. AIR SUPPLY FOR VARIOUS DEPTHS OF PACKING (Ref. 24)

20- and 24-foot depths were essentially the same for ammonia removals up to 90 percent. Higher removals up to 98 percent could only be obtained with the 24-feet of packing.

On the basis of this experience, a full-scale stripping tower was constructed at South Lake Tahoe. The tower was designed to remove 90 percent of the ammonia from 3-1/2 mgd of lime treated secondary effluent. Air flow is cross-flow while the water drips downward through the packing.

Initial operation of the stripping tower in the winter immediately revealed a limitation of ammonia stripping. The cold air contacting the wastewater resulted in icing on the slats. Moreover, since ammonia is more soluble in cold water than in warm water, more air was required to remove it. From theoretical considerations, difficulty with freezing may be expected when the wet-bulb temperature of the air is below 0°C. The large volumes of air used make heating uneconomic.

Another problem encountered with ammonia stripping is the formation of scale in the tower. Because the previously treated effluent is saturated with respect to calcium carbonate, contact with large volumes of air containing carbon dioxide precipitates calcium carbonate in the tower. In the case of the tower at Tahoe, the scale could be flushed from the tower except from inaccessible areas which could not be reached with a water jet. O'Farrell and Frauson (43) have described similar scaling difficulties encountered with ammonia stripping in a pilot desorption tower, except that, in contrast to the experience at Lake Tahoe, the scale was hard and adherent. The scale could only be removed from the packing grids by manual cleaning. However, a pilot tower has been operated in South Africa with scale so soft that the force of the water dripping through the tower fill has been sufficient to flush out the scale. Clearly the causes of the differences in the nature and amount of scale in various locations have not been resolved.

Cost of ammonia stripping, based on one year's operation at Lake Tahoe, has been reported by Evans and Wilson (44). The capital and operating cost, assuming continuous operation of a 7.5 mgd tower was

computed to be 1.8 cents/1000 gal. This cost does not include the cost of pH adjustment to 11.5 which is charged to phosphorus removal.

The concept of ammonia removal by air-stripping is technically and economically sound. Practical application must consider some restrictions. If 90 percent removal of ammonia nitrogen is required even in cold weather, provision must be made for increasing the air-to-water ratio which in turn can increase costs by about 50 percent. In below-freezing weather the tower will be inoperable. Design of the tower must consider ease of removal of accumulated solids.

A greater imponderable to the practical use of towers is the discharge of ammonia to the atmosphere. Because of the enormous dilution with air, the odor of ammonia cannot be detected. The concentration of ammonia is estimated to be 6700 $\mu g/m^3$ in the air exiting the tower. Questions can be raised, however, about the practice of transferring ammonia from a wastewater to the air. Locating a tower near a large body of water would not be recommended.

Selective Ion Exchange

Since ammonia exists in solution largely as the ammonium ion NH_4^+ at pH's less than about 9.5, removal can be obtained by conventional ion exchange methods. Synthetic ion exchange resins are uneconomic because of the problems of brine disposal and, more importantly, because of the selectivity of ion-exchange resins for other cations, principally divalent ions, which predominate in wastewaters. The selectivity of synthetic ion-exchange resins follows the Hofmeister or lyotropic series ($Ca^{++} > Mg^{++} > K^+ > NH_4^+ > Na^+$) which makes these exchangers inefficient in removing ammonia in the presence of divalent ions. Recent reports (45)(46) have shown that these problems may be minimized by using an ammonium selective zeolite such as clinoptilolite. Clinoptilolite is a naturally occurring zeolite which can be used after grinding and sieving to 20 x 50 mesh. The selectivity derives from the size of the pores and from the exchangeable cation sites located throughout the three-dimensional structure of the zeolite. The selectivity is in the order $K^+ > NH_4^+ > Na^+ > Ca^{++} > Mg^{++}$.

The combination of selectivity and an exchange capacity of about 2.0 meq/g make clinoptilolite a useful exchanger for ammonium ion in wastewater.

Following extensive laboratory work (45) a 100,000 gal per day demonstration pilot plant was constructed. The pilot plant consisted of a pretreatment plant, consisting of chemical flocculation and filtration, and an ion exchange-regeneration facility, which consisted of three 750 gal ion-exchange vessels and an ammonia stripping tower. Two columns were operated in series. When ammonia broke through in the first column, the third column containing freshly regenerated clinoptilolite was put on stream as the second column in series.

Breakthrough curves for two clinoptilolite columns with a bed volume of 500 gallons are shown in Fig. 15. Flow rate was 50 gpm of alum-coagulated secondary effluent containing an average of 16.3 mg/l NH_3-N. The first bed was operated alone until ammonia breakthrough was detected at a throughput of 75,000 gallons. At this point the second bed was placed in series with the first. Average ammonia removal was 97 percent for the 154,000 gallons processed and the average effluent ammonia nitrogen concentration was 0.53 mg/l.

The loaded clinoptilolite can be regenerated by any basic solution capable of obtaining a pH in excess of 11.0. Regenerants tested were solutions saturated with lime to raise the pH to about 12 and calcium chloride alone or supplemented with sodium chloride. The presence of a significant amount of Na^+ in the lime regenerant solution permits more rapid exchange for NH_4^+ than in the case where only Ca^{++} is available for exchange. Ammonia elution curves are shown in Fig. 16 for three different regenerant solutions (45). Regeneration with a mixture of $CaCl_2$ and NaCl in a saturated lime solution represents the most economic approach. The composition of this mixture is near that which results from continuous recycle of a regenerant solution (0.1N NaCl + $CaCl_2$) after air-stripping to remove ammonia. Following regeneration, the columns are rinsed with water to remove remaining regenerant and to reduce the pH to about 9.0.

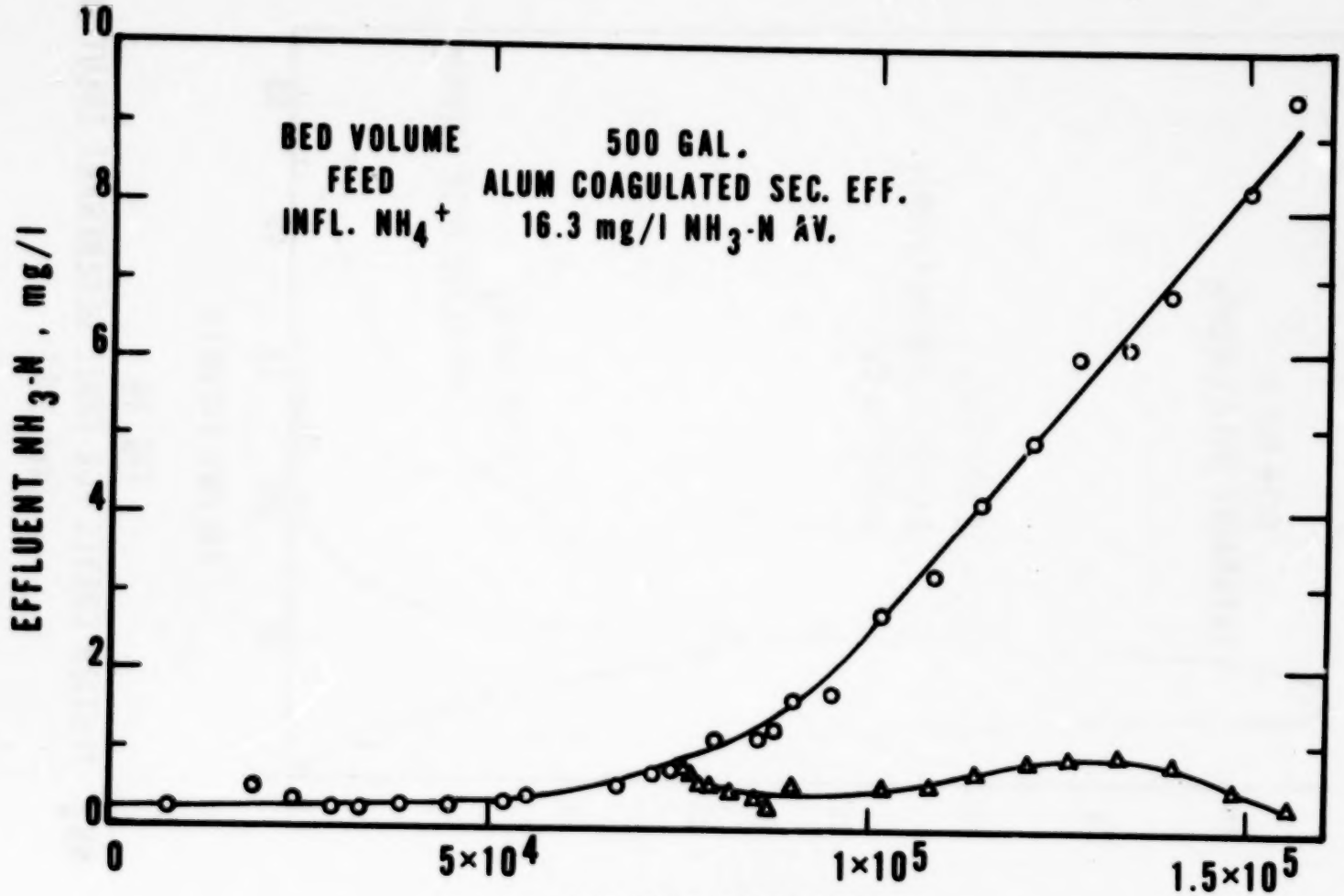

FIG. 15

AMMONIA BREAKTHROUGH CURVES FOR CLINOPTILOLITE COLUMNS (Ref. 45)

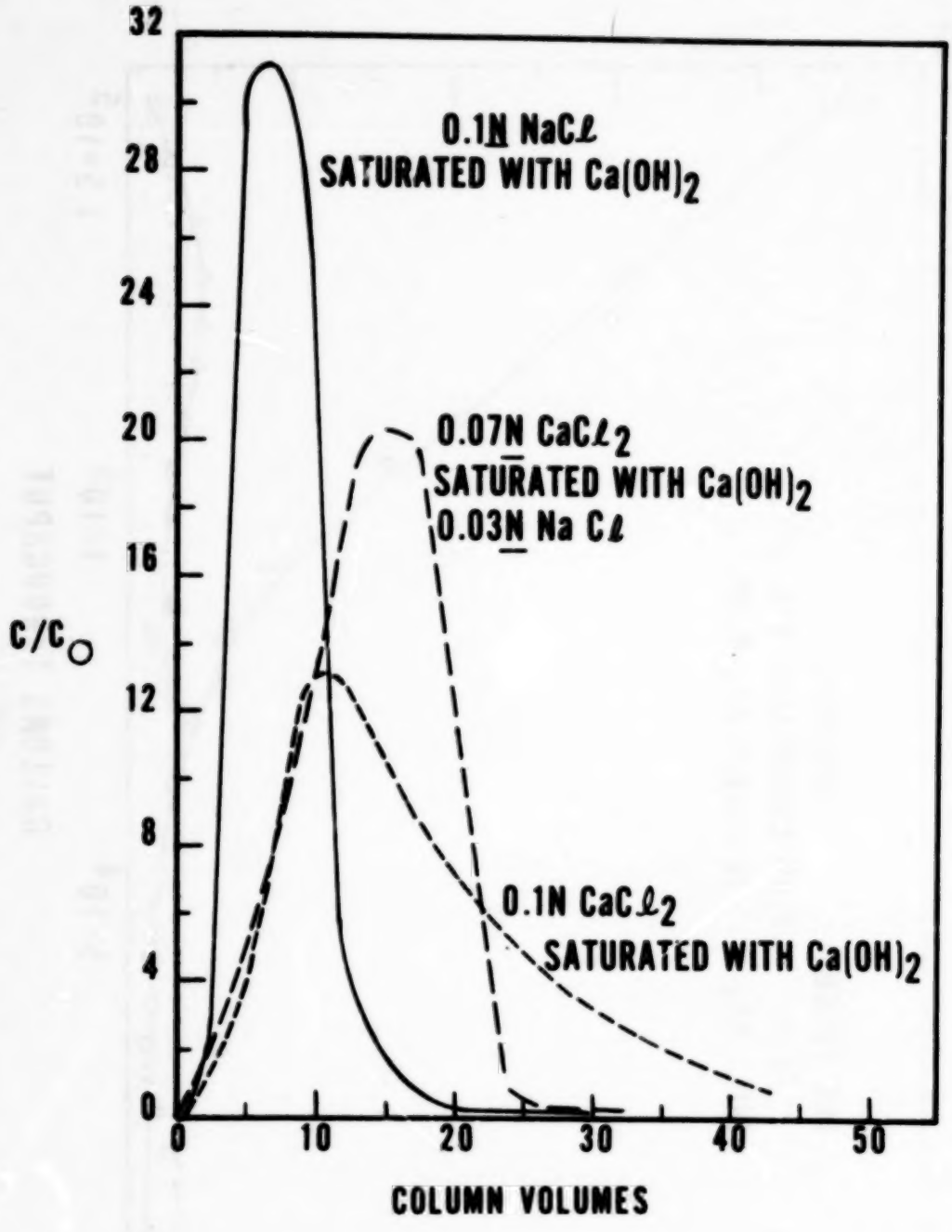

FIG. 16
NH_4^+ ELUTION CURVES FOR THREE REGENERANT SOLUTIONS
(Ref. 45)

More extensive studies on regeneration conditions were conducted by the University of California (47). Regeneration at pH 12.5 was found to be more effective than at pH 11.5 or 12.0. Higher pH's however, lead to dissolution of the clinoptilolite. Tests with an ammonia removal pilot plant showed average ammonia removal of 95.2 percent with an average effluent ammonia content of 0.53 mg/l NH_3-N.

The ammonia laden regenerant solution can be recycled after ammonia is removed by air-stripping. The problems of ammonia dispersal to the atmosphere are similar to those encountered in direct air-stripping of ammonia. But, since the ammonia content is 20 to 50 times as high and is contained in a much smaller volume of liquid, it is feasible to heat the air used for stripping and thus avoid the problem of freezing in cold weather. Because of the high concentration of ammonia, its odor is readily detectable in the effluent gas, although, of course, the total amount does not differ from that produced by direct stripping. Because under certain conditions there could be objections both to the odor and the discharge to the atmosphere of ammonia, other methods of removal of the ammonia from the regenerant solution are being sought. One method proposes oxidation of ammonia to nitrogen by electrochemical generation of chlorine.

Pilot studies at Battelle-Northwest (45) indicated a cost of between 3 and 6¢/1000 gal. An estimate prepared for a 7.5 mgd plant at Lake Tahoe showed 15¢/1000 gal. By comparison with other fixed adsorption methods, it is reasonable to suggest a cost of about 10¢/1000 gal for ammonia removal by zeolites. Firmer cost estimates must await more pilot operations.

Chlorine Oxidation of Ammonia

It has long been observed that breakpoint chlorination in water treatment practice has resulted in oxidation of ammonia (48). Basically, this concept provides a physical-chemical approach to removal of ammonia from wastewater. Much of the basic work on breakpoint chlorination has been done on river waters which nominally contain ammonia nitrogen concentrations below 1 mg/l N. An excellent review of the chemistry of reactions between ammonia and chlorine has been published in a series of papers by

Palin (49. It is only during the past two or three years that research has been undertaken on wastewaters with concentrations on the order of 10-20 mg/l NH_3-N. Whereas the objective of chlorination in water treatment is to disinfect and control odors, the objective in wastewater is to oxidize ammonia.

In the presence of aqueous ammonia, hypochlorous acid (aqueous solution of chlorine) will react to form a variety of chloramine compounds according to the following equations:

1. $Cl_2 + H_2O \leftrightarrows HOCl + H^+ + Cl^-$ hypochlorous acid
2. $NH_4^+ + HOCl \longrightarrow NH_2Cl + H_2O + H^+$ monochloramine
3. $NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$ dichloramine
4. $NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$ trichloramine

While the above equations represent the stoichiometry of the chlorine-ammonia reactions, the relative concentrations of each of the species is determined by the ratio of initial molar concentrations of chlorine and ammonia, which determines the rates of reaction and, more importantly, by the pH of the system. Reactions with organic material and other nitrogen compounds also occur but are of relatively minor importance in chlorine consumed.

Several reactions have been suggested to explain the decrease in chlorine residual when increasing amounts of chlorine are added to a solution containing ammonia, i.e., the breakpoint curve. Palin (49) suggests that two reactions predominate, at least in the concentrations found in water treatment practice. Thes equations are:

5. $NH_2Cl + NHCl_2 \longrightarrow N_2 + 3\ H^+ + 3\ Cl^-$
6. $2\ NH_2Cl + HOCl \longrightarrow N_2 + 3\ H^+ + 3\ Cl^- + H_2O$

According to these equations, the stoichiometric ratio of chlorine to ammonia nitrogen at the breakpoint would be 7.6 to 1 by weight. Observed ratios approach 8-9 to 1 as a result of side reactions. In practice, breakpoint chlorination of wastewater does not quite follow the simple paths

represented by the above equations. The reactions become very much more complicated and much additional research is needed to identify the multiple interactions and reaction products of chlorine and ammonia. Nevertheless, recent work by Pressley, et al. (50), Lawrence, et al. (51) and Cassel, et al. (52) has shown that oxidation of ammonia by chlorine is technically feasible. Undesirable side reactions can be controlled so that the principal end-products of the overall reaction is the desired nitrogen gas, resulting in almost total removal of ammonia nitrogen.

A laboratory study of the breakpoint process for ammonia removal was conducted at the Environmental Protection Agency Washington, D.C. Pilot Plant and has been described by Pressley, et al. (50). Addition of chlorine to buffered solutions of ammonia at various pH's resulted in the typical breakpoint curves shown in Fig. 17. At a pH of 7.0 the breakpoint occurred at nearly the stoichiometric ratio of approximately 8:1 weight ratio of $Cl:NH_3$-N. At pH's outside of this range, increased amounts of chlorine were required for breakpoint and total residual chlorine in the product increased. Palin (49) has offered an explanation of the typical breakpoint curve. In the ascending branch of the curve the chlorine is present in combination with ammonia as mono-and-dichloramine. The peak of the curve represents the point where all the ammonia initially present is combined to form the chloramines. In the presence of excess chlorine, the chloramines are unstable and react with free chlorine with the net result that the amount of available chlorine is decreased. This accounts for the descending leg of the curve. When all the chloramines have been converted to such a form that will no longer react with free chlorine, the further addition of chlorine causes a proportionate rise in residual chlorine. This accounts for the ascending branch of the curve. The simple overall reaction of chlorine with ammonia can be expressed by the following equation:

7. $2\ NH_3 + 3\ Cl_2 \text{ ------> } N_2 + 6\ HCl$

From the equation,it can be seen that the final products of the reaction at the breakpoint are nitrogen gas and hydrochloric acid. Also,

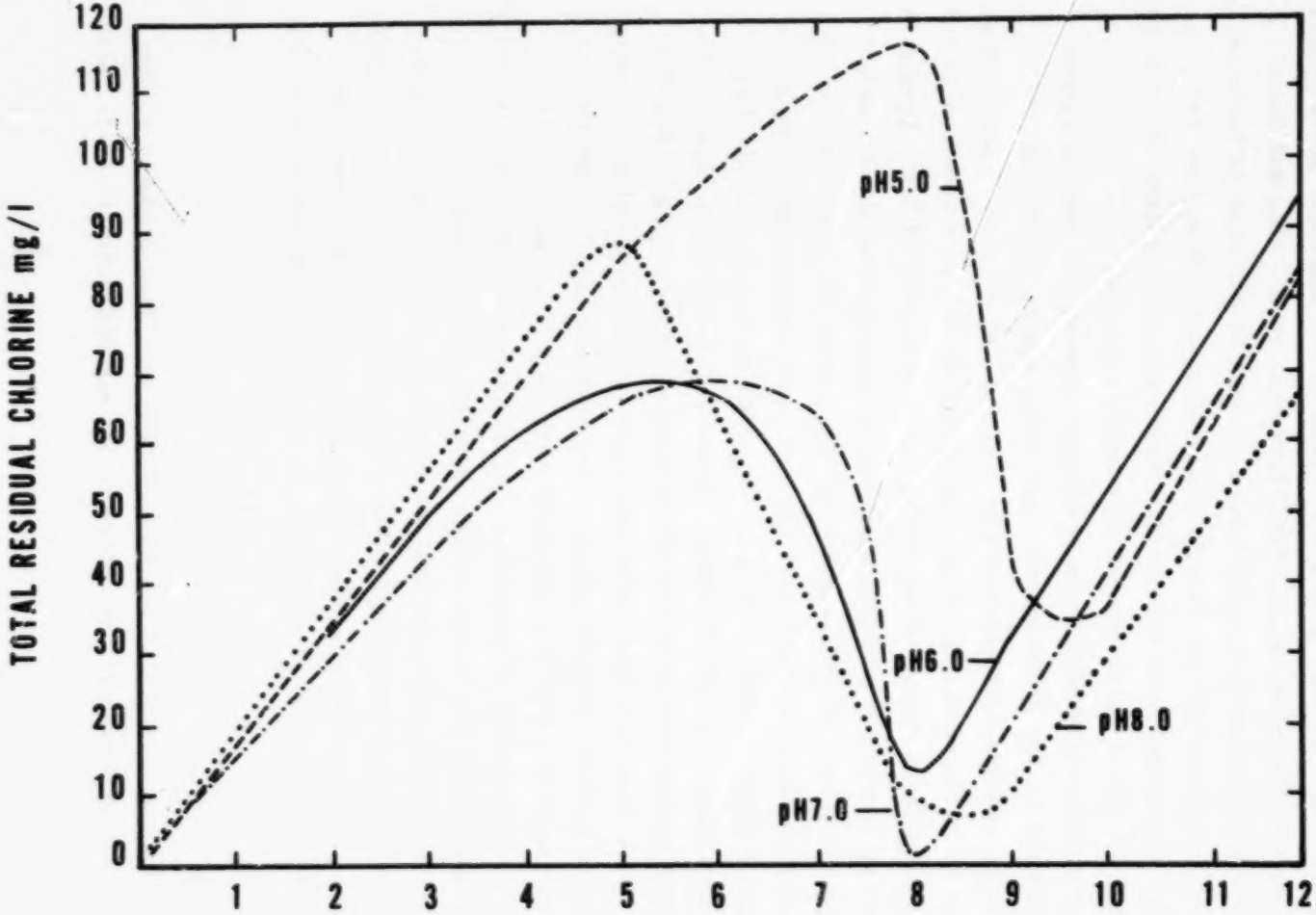

FIG. 17

BREAKPOINT CHLORINATION AT DIFFERENT pH'S (Ref. 50)

this is the equation that is normally used to calculate the stoichiometric weight of chlorine to oxidize ammonia nitrogen, which is generally stated to be 7.6 parts of chlorine per part of ammonia nitrogen.

Analyses of the gas evolved from the reaction of chlorine and ammonia at the breakpoint ratio have shown that only N_2 is produced (50). The off-gas was analyzed for N_2, O_2, N_2O, NO and NO_2. Analyses of the solution, however, revealed that undesirable side reactions occur leading to the formation of nitrate and trichloramine (nitrogen trichloride). The formation of these end products has been shown by Pressley (50) to be a function of pH, as shown in Fig. 18. At pH's greater than 6.0 nitrate formation increases and can attain a concentration as high as 2.0 mg/l NO_3-N. At pH's less than 7.0, nitrogen trichloride is produced and can attain concentrations in excess of 2.0 mg/l of NCl_3-N.

Nitrogen chloride is a volatile oil with a pungent odor resembling chlorine. Its vapor attacks the eyes and mucous membranes and is most undesirable in a product water. Its formation, however, can be controlled by maintaining the pH in excess of 7.0. The concentration is negligible, 0.05 mg/l NCl_3-N, at pH 8.0. Nitrogen trichloride is unstable and on standing hydrolyzes to ammonia and hypochlorous acid.

The reactions of chlorine with ammonia are rapid and essentially unaffected by temperature (53). Breakpoint tests at pH 6.0 in the temperature range of 5-40°C have not revealed significant changes in reaction products after two hours contact time.

The overall reaction, equation 7, indicates that substantial amounts of hydrochloric acid are produced. Stoichiometrically, 14.3 mg/l of $CaCO_3$ alkalinity are required to neutralize the acid produced by the oxidation of 1 mg/l NH_3-N to N_2. Thus, a wastewater containing 15 mg/l NH_3-N will consume an alkalinity of about 215 mg/l. To avoid the formation of undesirable nitrogen trichloride and to maintain a product water in the range of pH 6-7, additional alkalinity will have to be added if insufficient alkalinity is not already present.

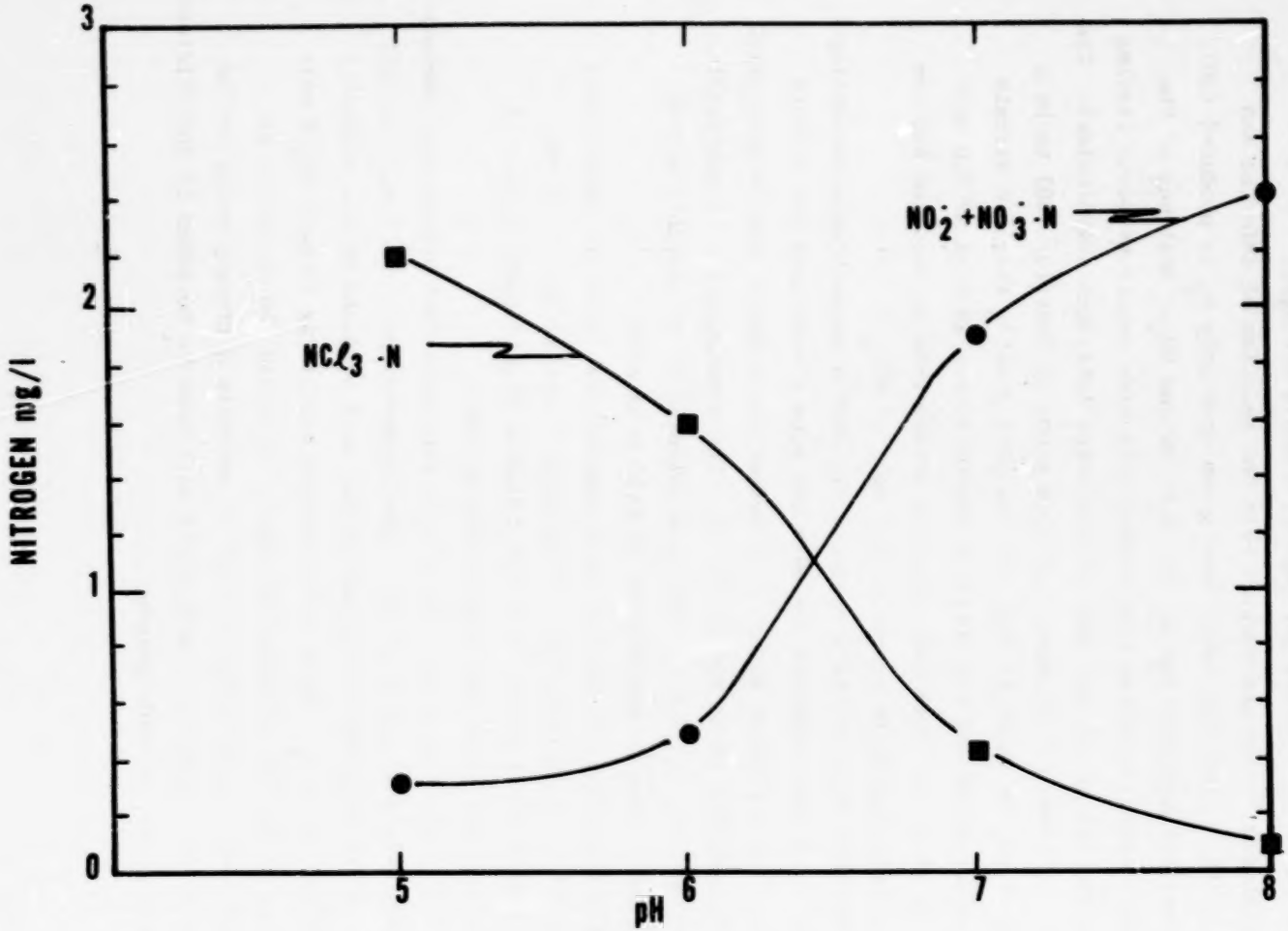

FIG. 18
EFFECT OF pH ON $NO_2^- \cdot NO_3^-$
AND $NC\ell_3$ FORMATION (Ref. 50)

At precisely the breakpoint, the treated solution should contain no chlorine or chloramines, and ammonia nitrogen should be absent. In practical terms, however, precise pacing of chlorine addition with ammonia nitrogen content will not be possible. To avoid discharging a product water containing free chlorine, chloramines or chlorinated organic compounds, the treatment system generally will include some type of dechlorination process. Magee (54) in his excellent review of dechlorination on activated carbon showed that free chlorine is effectively reduced on the carbon. Moreover, the "life" of the carbon is extremely long. Activated carbon dechlorination plants accepting chlorinated river waters have been in operation for seven to eighteen years with no appreciable decline in activity. Recent work (51)(55) has shown that free chlorine is totally reduced by activated carbon. The evidence on removal of chloramines is less clear, and it is obvious that more research is needed to determine the fate of chloramines when applied to activated carbon.

Overall, ammonia nitrogen removal by breakpoint chlorination is technically feasible. In the range of pH 6.5 to 7.5, 95-99 percent of the ammonia can be oxidized to nitrogen gas. Capital costs for the process would be small, and the principal cost of the process is the cost for chlorine and a small additional cost of lime for alkalinity. Thus, for an effluent containing 15 mg/l NH_3-N, approximately 120 mg/l of chlorine would be required. At $0.04/lb, the cost for chlorine would be $0.038/1000 gal of treated water. Since breakpoint chlorination is a most effective disinfection process, part of the cost of ammonia removal can be credited to disinfection.

Two principal disadvantages can be cited for breakpoint chlorination. Chlorides are added to the product water; each milligram of chlorine added is reduced to chloride ion and for pH controlled situations, an equivalent quantity of cation is added. For an initial ammonia-nitrogen concentration of 15 mg/l, the increment in total dissolved solids (caustic added for pH control), could be 240 mg/l. Where additional total dissolved solids in

the product water are objectionable, then this process should not be considered. Also, large amounts of liquid chlorine must be transported and handled. A solution to this dilemma, however, is on-site electrolytic production of sodium hypochlorite. Electrochemical production of sodium hypochlorite has been practiced for sewage chlorination and treatment for years, Marson (56). The process, however, needs to be optimized for breakpoint treatment.

Summary

Phosphorus, an important nutrient in eutrophication, can be removed from wastewater. Alternatives are available as to precipitant to use and as to location in a treatment system. Removals in excess of 95 percent can be achieved. The cost is reasonable and application at full scale is proceeding.

Nitrogen compounds, which are nutrients as well as objectionable pollutants, also can be removed from wastewater. Three physical-chemical processes are in various stages of development. Removals in excess of 90-95 percent appear to be obtainable. Application at full-scale needs some additional pilot plant study.

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